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Rigidified tetrathiafulvalene–[60]fullerene assemblies: towards the control of through-space orientation between both electroactive units

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Our recent works on fused TTF–C_{60} dyads, $(TTF)_n$–C_{60} polyads and C_{60}–TTF–C_{60} dumbbell triads in which the acceptor C_{60} is doubly tethered to the donor tetrathiafulvalene through a rigidified cyclohexene ring are presented. This approach was developed in order to control the relative orientation as well as the distance between both donor and acceptor entities. Thereby, through-space interactions which are of great importance for photoinduced electron- and/or energy-transfer processes are expected to dominate because of the special topology of the molecules. The two linked C_{60} and TTF chromophores in such adducts are not only in close proximity but also have optimal orbital orientations, thus facilitating these through-space electronic interactions. These new C_{60}-based assemblies were synthesized by [4 + 2] Diels–Alder cycloaddition reactions. The different methodologies considered for their synthesis are discussed, their analytical, spectroscopic characterizations and electrochemical properties are also described. The selective electro-oxidation or reduction afforded the corresponding radical cation and radical anion which were characterized by EPR. These C_{60}-based assemblies were studied for their nonlinear optical and optical limiting applications. Moreover, intramolecular photoinduced charge-separation and charge-recombination processes in a fused C_{60}–TTF–C_{60} dumbbell triad which was designed to be soluble in organic solvents were investigated by time-resolved absorption and fluorescence techniques. Appreciable interaction between the C_{60} moiety and TTF moiety in the ground state was suggested by steady-state absorption spectra and the fluorescence spectra showed considerable interaction in the singlet excited state. The nanosecond transient absorption spectra displayed the formation of the charge-separated radical pair C_{60}–$TTF^{\bullet +}$–$C_{60}^{\bullet -}$, characterized by a lifetime of *ca.* 20 ns in benzonitrile.

Introduction

Since the discovery of fullerene C_{60}[1] and techniques for its large scale preparation,[2] the development of molecular and supramolecular[3] chemistry of C_{60} has emerged as a promising field in materials science. In particular, fullerene C_{60} underwent a rapid development of the covalent chemical functionalization of this carbon sphere with the aim of generating many new fullerene-based materials.[4] Consequently, the possibility of modifying fullerenes has made C_{60} a very exciting molecule to build up new molecular assemblies with remarkable physical and chemical properties on a preparative scale. Moreover, C_{60} was discovered as a very attractive electron acceptor with unique electrochemical properties.[5] This peculiarity was attributed to its ability to accept up to six electrons per molecule, its unique three dimensional delocalised π-electron system with a high I_h symmetry. This electron-accepting character combined with photophysical properties[6] make C_{60} a very promising chromophore in photodriven redox processes. Thus, C_{60} derivatives could interact with π-donor polymers giving rise to long-lived photoexcited species which are useful in the conversion of solar energy.[7]

By analogy, considerable efforts were devoted in recent years to the development of systems in which C_{60} is covalently linked to an electron donor.[8] Such molecular assemblies are of particular interest in that they can exhibit characteristic electronic and excited-state properties,[6] which make them promising candidates for the investigation of photoinduced electron transfer processes and long-lived charge-separated states $D^{\bullet +}$–$C_{60}^{\bullet -}$.[9] In fact, C_{60} gives rise in electron-transfer processes to a rapid photoinduced charge separation and a further slow charge recombination in the dark.[10] It was proposed that this peculiar effect of fullerenes in electron transfer could be ascribed to the small reorganization energies of fullerenes. That could explain the acceleration effect of photoinduced charge separation as well as charge shift and the deceleration effect of charge recombination in donor-linked fullerenes.[11]

These unique and remarkable properties make novel organofullerenes containing electron-donor moieties very interesting targets. These are designed with the intention of synthesizing arrays that exhibit optimized electron transfer kinetics and minimize loss of excited-state energy of back-electron transfer. Up to now, several electron-donor fragments have been attached to the C_{60} cage and some of these assemblies are the basis for the design of artificial photosynthetic systems with the objective to mimic the primary events in natural photosynthesis.[12] This behaviour of C_{60} in intramolecular processes involving electron or energy transfer between both electroactive entities has also evoked interest for potential applications for molecular electronic devices,[13] systems exhibiting nonlinear optical[14] or optical limiting[15] properties and the realization of photovoltaic cells with the aim of achieving efficient conversion of solar energy.[16]

Among the wide variety of donor molecules that have been recently linked to C_{60} (ferrocene,[17] porphyrin,[18] phthalocyanin,[19] transition metal complexes,[20] aniline derivatives,[21] polycondensed aromatics,[22] carotenoids,[23] oligoarylene[24] and

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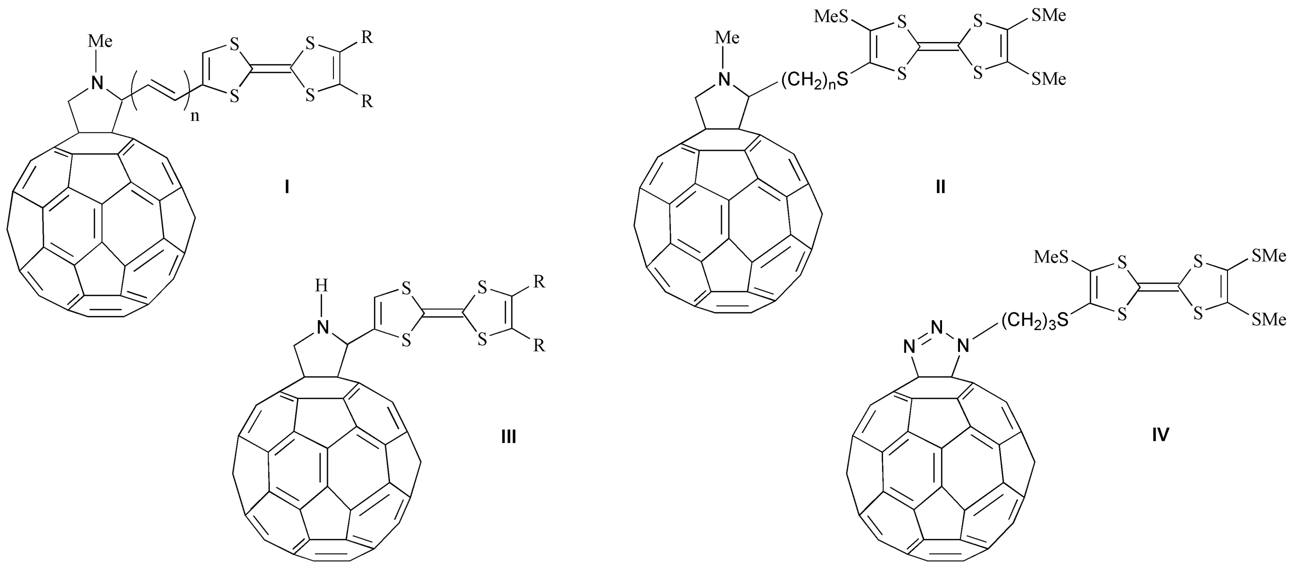
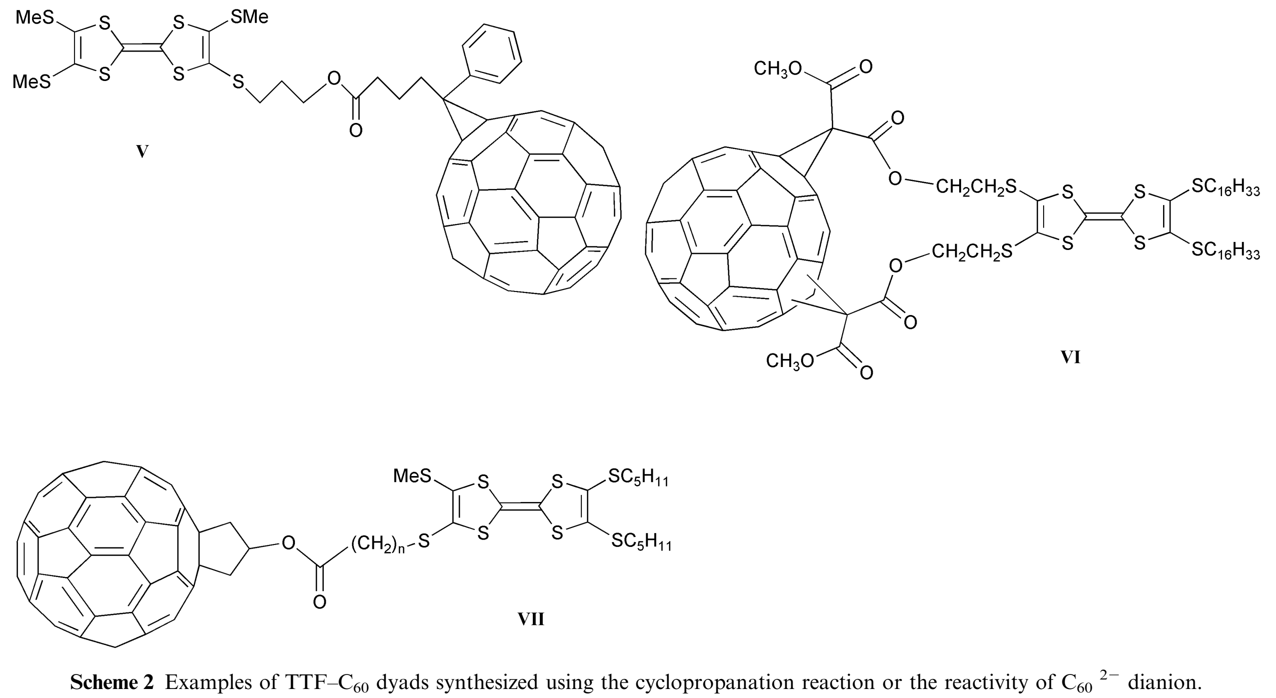


Scheme 1 Examples of TTF–C_{60} dyads synthesized through 1,3-dipolar cycloaddition.

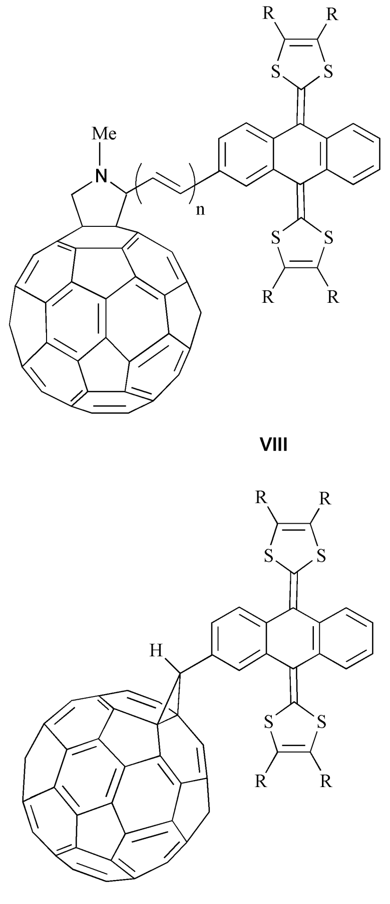
oligothiophene[25]), it should be pointed out that most of these donors present an aromatic character in the ground state, which is partially or totally lost upon oxidation yielding a π-radical cation species. On these grounds, the strong donor tetrathiafulvalene (TTF) has emerged as an interesting class of compound in the light of increasing stabilization of the charge-separated state $TTF^{\bullet +}$–$C_{60}{}^{\bullet -}$.[26] This peculiarity is due to the gain of aromaticity as a result of the formation of the thermodynamically very stable heteroaromatic 1,3-dithiolium cation(s) upon oxidation(s) of the TTF molecule which is non-aromatic in its ground state configuration.[9b,27] On this basis, TTF derivatives have been covalently linked to C_{60} through a flexible spacer using several methodologies. The 1,3-dipolar cycloaddition following Prato's procedure appeared as one of the most developed strategies.[28] This involved the *in situ* generation of an azomethine ylide formed from sarcosine (*N*-methylglycine) and the corresponding aldehyde. The following 1,3-dipolar cycloaddition to C_{60} occurring at the [6,6]-junction of the C_{60} cage afforded dyads **I**[29] and **II**[30] which present for some of them efficient photoinduced charge-separation yielding ion-radical pairs (Scheme 1).[26] This methodology was also extended to the synthesis of fulleropyrrolidine dyad **III**[31] (using glycine instead of sarcosine) and fullerotriazoline **IV** obtained by cycloaddition of the azide derivative to C_{60}.[32]

The cyclopropanation reaction was also used as a powerful tool to prepare C_{60}-based dyads such as **V**[33] and **VI**[34] (Scheme 2). In the latter case, it was announced that paramagnetic signals were shown by EPR at room temperature without photoinduction, indicating efficient intramolecular electron transfer between both electroactive units. Recently, the chemical reactivity of the $C_{60}{}^{2-}$ dianion was applied to give rise to new C_{60}-based assemblies **VII** using the 1,2-fused cyclopentanol-C_{60} as starting material.[35]

The remarkable effect concerning the lifetime of the charge-separated radical pair $TTF^{\bullet +}$–$C_{60}{}^{\bullet -}$ was recently completed by the introduction of the concept involving both the gain of aromaticity and the gain of planarity. In particular, the geometries in π-extended tetrathiafulvalene derivatives such as dyads **VIII**[36] and **IX**[27a] (Scheme 3) with *p*-quinonoid structures reveal highly distorted conformations, by adopting a butterfly-shaped structure in the ground state to avoid contacts between



Scheme 2 Examples of TTF–C_{60} dyads synthesized using the cyclopropanation reaction or the reactivity of $C_{60}{}^{2-}$ dianion.



VIII

IX

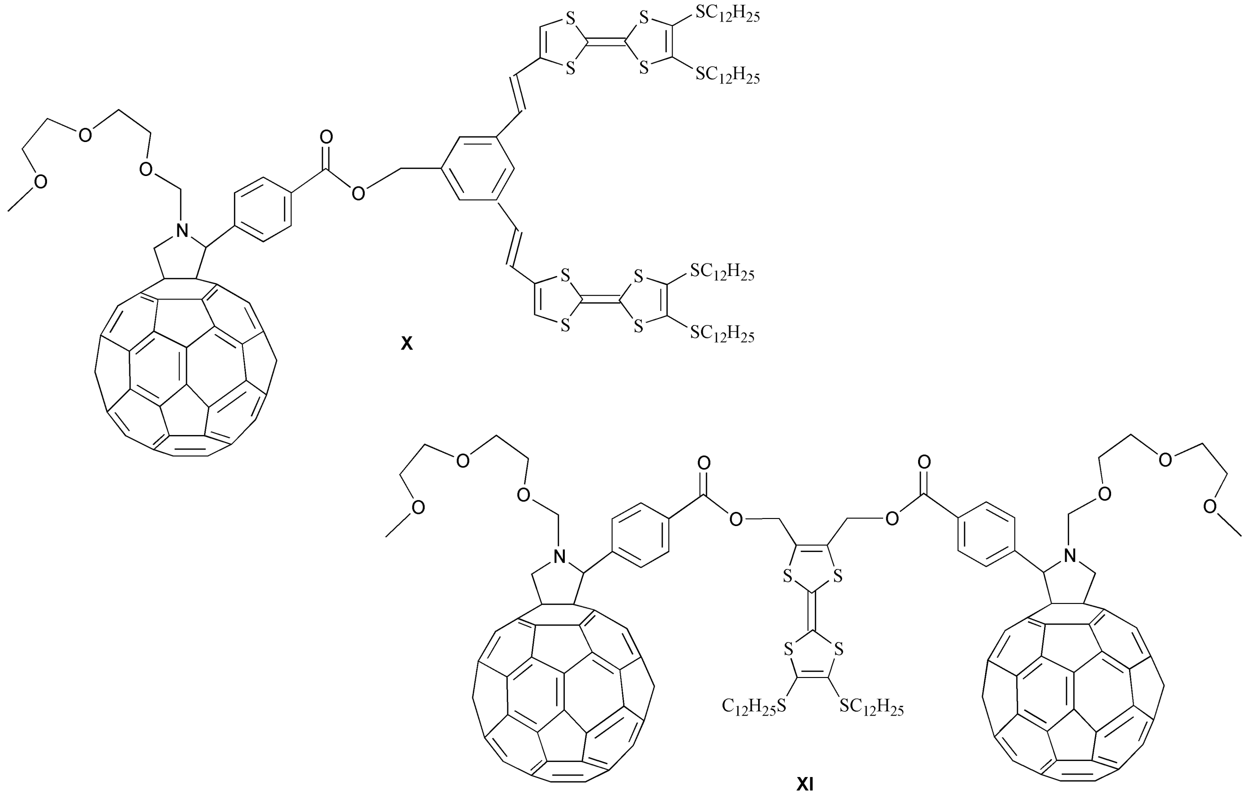
Scheme 3 Examples of C_{60}-(π-extended)TTF assemblies.

sulfur atoms of the TTF core and the *peri*-hydrogen atoms of the benzene ring. These geometrical features of *p*-quinodimethane analogues of TTF have a strong impact on the stabilization of the charge-separated state. In this case, the lifetimes of the charge-separated states in C_{60}–(π-extended)TTF dyads **VIII** were increased thanks to the increased stability of the $C_{60}^{\bullet -}$–(π-extended)$TTF^{\bullet +}$ pair with the stabilization of the donor and the gain of aromaticity and planarity associated with this oxidation.[36]

These different synthetic methodologies allowed the rapid development of more and more sophisticated C_{60}-based molecular assemblies. Thus, TTF–C_{60}–TTF triad **X**[37] and C_{60}–TTF–C_{60} triad **XI**[38] were designed with the aim of yielding increasing interactions between the chromophores in the ground state and long-lived charge-separated radical pair (Scheme 4).

In all these cases of fullerene–spacer–donor systems, intramolecular electronic interactions can be either through space or through intervening bonds. Following another strategy which consists in controlling the relative orientation as well as the distance between both counterparts, we have designed assemblies in which the TTF unit is bound to the three dimensional electron acceptor C_{60} by a rigid spacer. Thereby, through-space interactions which are of great importance for photoinduced electron- and/or energy-transfer processes are expected to dominate because of the special topology of the molecules. The two chromophores in such C_{60}-based systems are not only in close proximity but also have optimal orbital orientations, thus facilitating these through-space electronic interactions. In fact, recently the importance of the orientation between electron donors and acceptors in the electron transfer that takes place in a C_{60}–porphyrin dyad has been shown.[18v] The method of choice for the synthesis of such TTF–C_{60} rigidified systems consists in using the [4 + 2] Diels–Alder cycloaddition of C_{60} (Scheme 5).

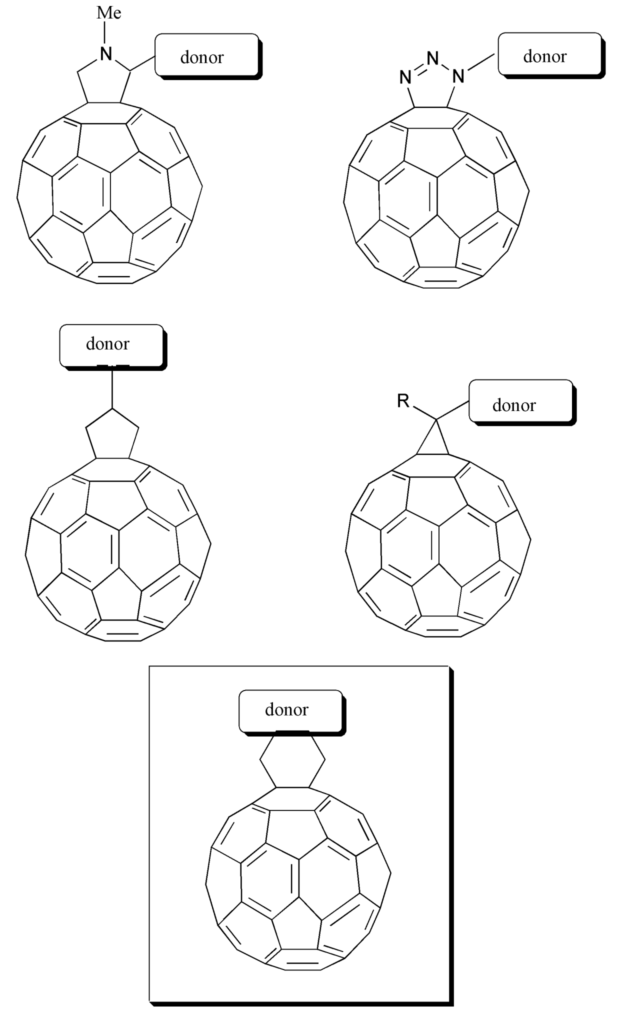
In our quest for the construction of such new rigidified molecular donor–acceptor (D-A) assemblies and with the aim of promoting an intramolecular electron transfer between both antagonistic redox counterparts, we have designed target molecules **1** and **2**, in which TTF is tethered by a cyclohexene ring to one or two C_{60} molecules (Scheme 6). Consequently, the fusion of these two electroactive centres with a six-membered ring provides not only a short distance, but also a rigid spacer



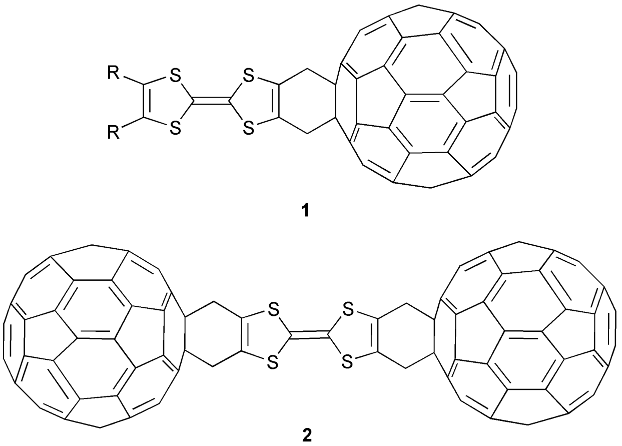
X

XI

Scheme 4 Examples of TTF–C_{60}–TTF and C_{60}–TTF- C_{60} triads.



Scheme 5 Strategies to build up donor–C_{60} assemblies.



1

2

Scheme 6 TTF–C_{60} and C_{60}–TTF–C_{60} target molecules.

between the donor and the acceptor, giving rise to a well-defined spacing and orientation with respect to each other. This kind of bridge has proven to be very efficient for mediating in electron- and energy-transfer between two electroactive centres through-bond coupling mechanism regardless of its length.[21a–c]

We herein report the detailed description of the methodology we have developed for the synthesis of TTF–C_{60} dyads, $(TTF)_n$–C_{60} polyads and C_{60}–TTF–C_{60} dumbbell assemblies. These different materials were characterized by usual spectroscopic and electrochemical methods. Radical-ion systems were electrochemically generated and studied by EPR spectroscopy. Moreover, nonlinear optical and optical limiting properties, as well as preliminary results on the photophysical behaviour of some of these systems are presented.

Results and discussion

Strategy of synthesis

The retrosynthetic analysis of such assemblies indicates that two different routes could be considered: *i*) the disconnection of the TTF central double bond leading to 1,3-dithiole derivatives. The corresponding 2-oxo-(or 2-thioxo or 2-selenoxo)-1,3-dithioles **3** or dithiolium salts **4** could form by coupling the TTF core according to well known procedures;[39] *ii*) the disconnection of the cyclohexene ring leading to a [4 + 2] Diels–Alder cycloaddition since C_{60} is known as an acceptor comparable to *p*-benzoquinone and naphthoquinone and as a good dienophile (Scheme 7).

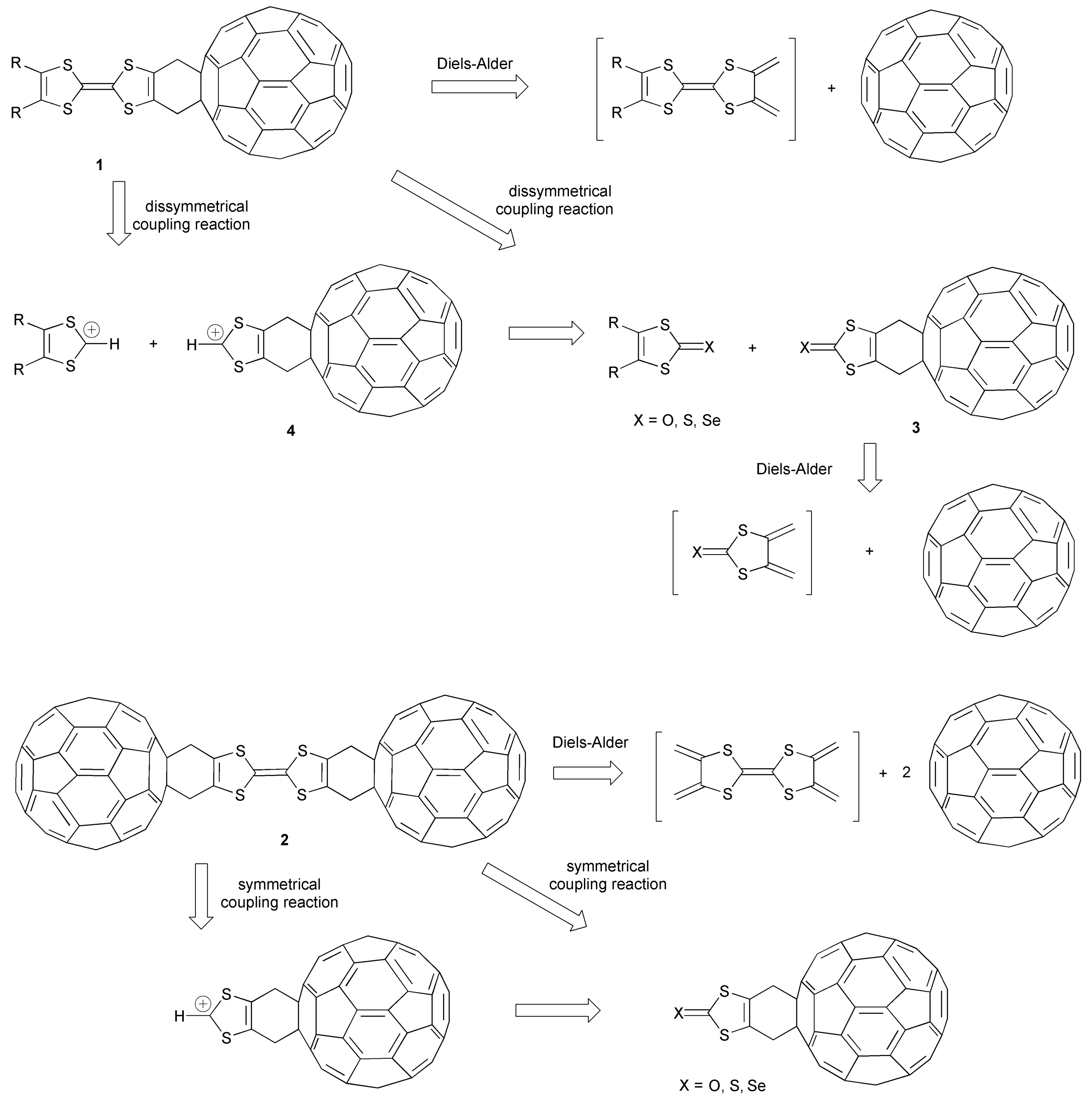
Consequently, the different approaches revealed that the key intermediates are the corresponding dienes **5**, **6** and **7** (Scheme 8) which constitute heteroatomic analogues of *o*-quinodimethane[40] and are expected to react efficiently with C_{60}. While the synthesis of new π-electron donors based on the TTF core has been particularly fruitful and varied, the possibility of developing chemistry in this family from a diene group able to react through a Diels–Alder cycloaddition was surprisingly missing. Clearly this research area has been restricted by lack of suitable TTF building blocks and to our knowledge, only Rovira *et al.* have previously contributed to this field.[41] This approach, developed in Barcelona, used a sulfone group as the diene precursor, the latter being formed *in situ* by thermal extrusion of sulfur dioxide. This methodology was successfully applied, independently and simultaneously to the work carried out in Angers, to realize cycloadditions of 2,3-dimethylidene[*2H*]-TTF derivatives **6** to C_{60}, the TTF core being substituted with substituents R = H, CH_3 or CO_2CH_3.[42] Nevertheless, no evidence for the formation of cycloadducts from tetramethylidene[*4H*]-TTF **7** with C_{60} was observed probably due to the drastic experimental conditions responsible for the polymerization of bis-diene **7**.

Angers' approach was based on the synthesis of precursors which could smoothly generate the formation of these transient dienes. In this context, we have chosen the novel vicinal bis(bromomethyl)-2-oxo(or 2-thioxo or 2-selenoxo)-1,3-dithioles **8** and bis and tetrakis(bromomethyl)TTFs, **9** and **10**, able to undergo a reductive elimination upon treatment with naked iodide to give rise to dienes **5**, **6** and **7** respectively. This kind of reaction and its mechanism were initially proposed by Cava *et al.* in non-heterocyclic series (Scheme 9).[43] We should note that these compounds **8**–**10** are of significant interest for their synthetic applications as versatile building blocks for the selective functionalization of the TTF core.

Synthesis of fused 2-oxo(or thioxo or selenoxo)-1,3-dithiole-C_{60} systems

Historically, we have focused our attention on the synthesis of 2-oxo and 2-thioxo-1,3-dithiole C_{60}-based cycloadducts.[44] First, in order to generate 2-oxo intermediate **3a**, we compared two different pathways (Scheme 10): the thermal rearrangement of *S*-propargyl xanthate **11**[45] (Route A) and the reductive 1,4-elimination of the corresponding 2-oxo-4,5-bis(bromomethyl)-1,3-dithiole **8a**[46] prepared from 2-oxo-4,5-dimethyl-1,3-dithiole **12** (Route B).

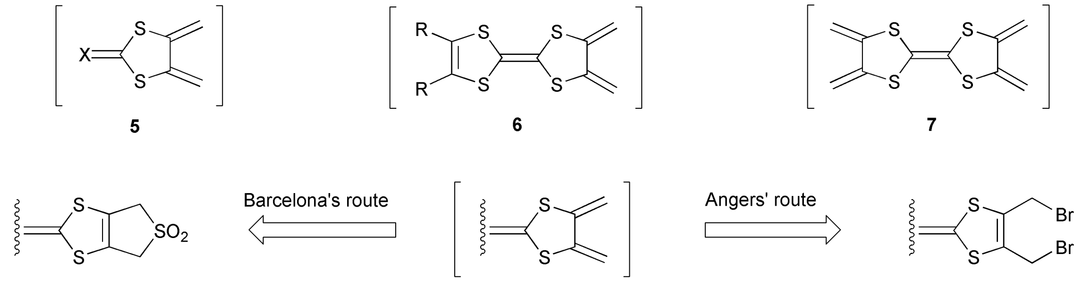
The route using xanthate **11** as starting material appeared to be the more efficient, affording the monoadduct in 60% yield. Di- and triadducts could also be separated by silica gel column chromatography and characterized in 5–10% and <5% yields respectively. Route B used potassium iodide in the presence of 18-crown-6 to *in situ* generate diene **5a** according to a method previously developed by Müllen *et al.*[47] The expected monocycloadduct of C_{60} **3a** was obtained in 45% yield, di- and



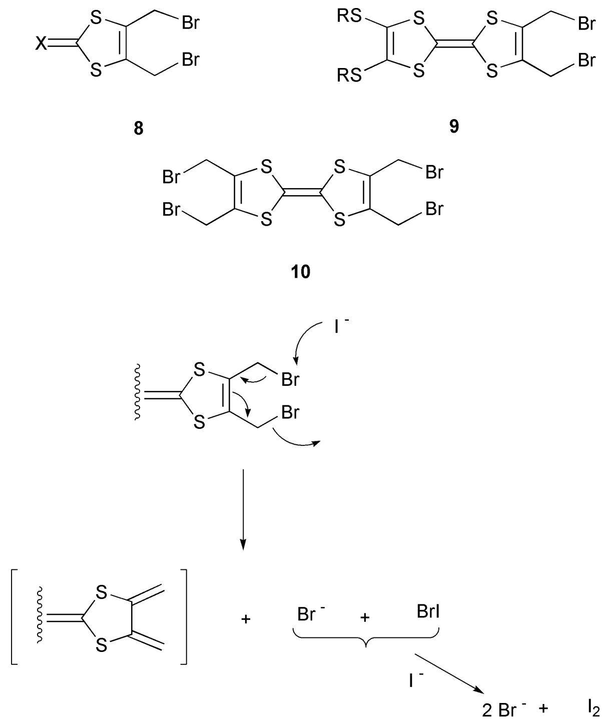
Scheme 7 Retrosynthetic analyses of TTF–C_{60} dyads **1** and C_{60}–TTF– C_{60} dumbbell **2**.

triadducts being also isolated and characterized by mass spectrometry.

In order to reach the corresponding cycloadduct **3b**, we applied route B to the 2-thioxo series. So we had to prepare the starting material 2-thioxo-4,5-bis(bromomethyl)-1,3-dithiole **8b** on a large scale. Thus, reaction of phosphorus tribromide on 4,5-bis(hydroxymethyl)-2-thioxo-1,3-dithiole **13a**[48] readily gave **8b** in excellent yield.[49] Similarly, the application of route B (potassium iodide and 18-crown-6) to **8b** gave adduct **3b** in 38% yield. Surprisingly, we noted the presence of the oxo-derivative **3a** which was isolated in 15–20% yield. In addition, treatment of 2-oxo-1,3-dithiole **3a** with a sodium methoxide methanolic solution gave the disodium dithiolate intermediate which was trapped by thiophosgene, leading to **3b** in 60% yield.[44]



Scheme 8 Routes to prepare the heterocyclic dienes.



Scheme 9 Structures of bis and tetrakis(bromomethyl) derivatives and mechanism proposed for the reductive elimination using iodide anion.

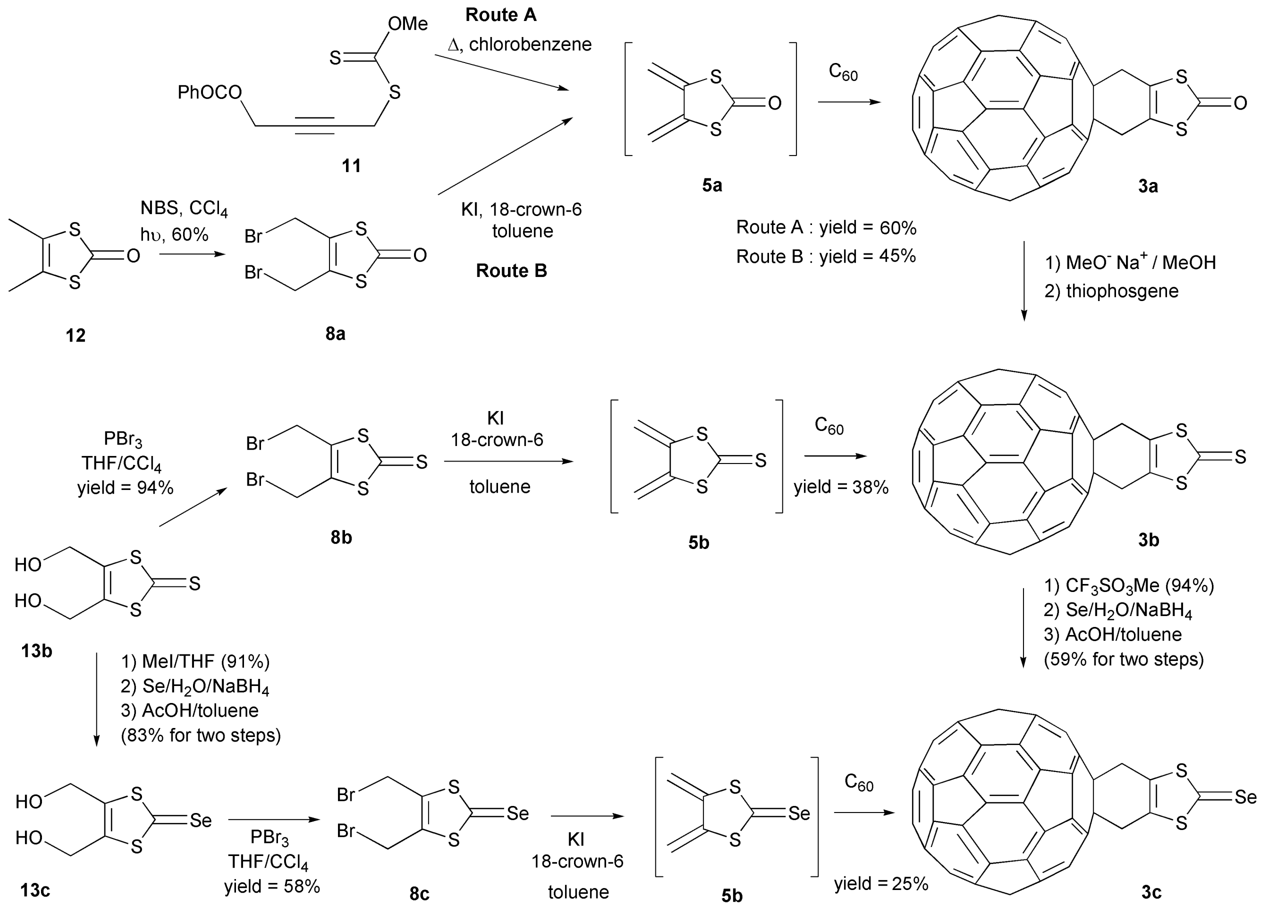
The synthesis of selenoxo derivative **3c** started from the same compound **13b**. After the conversion to the 1,3-dithiolium salt by methylation, the treatment to reach 4,5-bis(hydroxymethyl)-2-selenoxo-1,3-dithiole **13c** was achieved according to a previously described methodology.[50] Thus, reaction using phosphorus tribromide readily gave compound **8c** which was used for the preparation of the fused 2-selenoxo-1,3-dithiole-C_{60} assembly **3c** (2-oxo-1,3-dithiole-C_{60} adduct **3a** was also isolated in 20–30% yield). The efficient route, which was previously used to transform **13b** into **13c**, was applied to convert **3b** into the analogous selenoxo derivative **3c**.

Unfortunately, attempts to achieve the symmetrical trialkyl phosphite-mediated coupling reactions from these different 1,3-dithiole-C_{60} systems **3a**, **b**, **c** into dumbbell **2** failed, as did the dicobalt octacarbonyl method from **3b**.[51] Dissymmetrical coupling involving other 2-(thi)oxo-1,3-dithioles were also unsuccessful. These results are in agreement with those recently published by the group of Rovira *et al.*[42b]

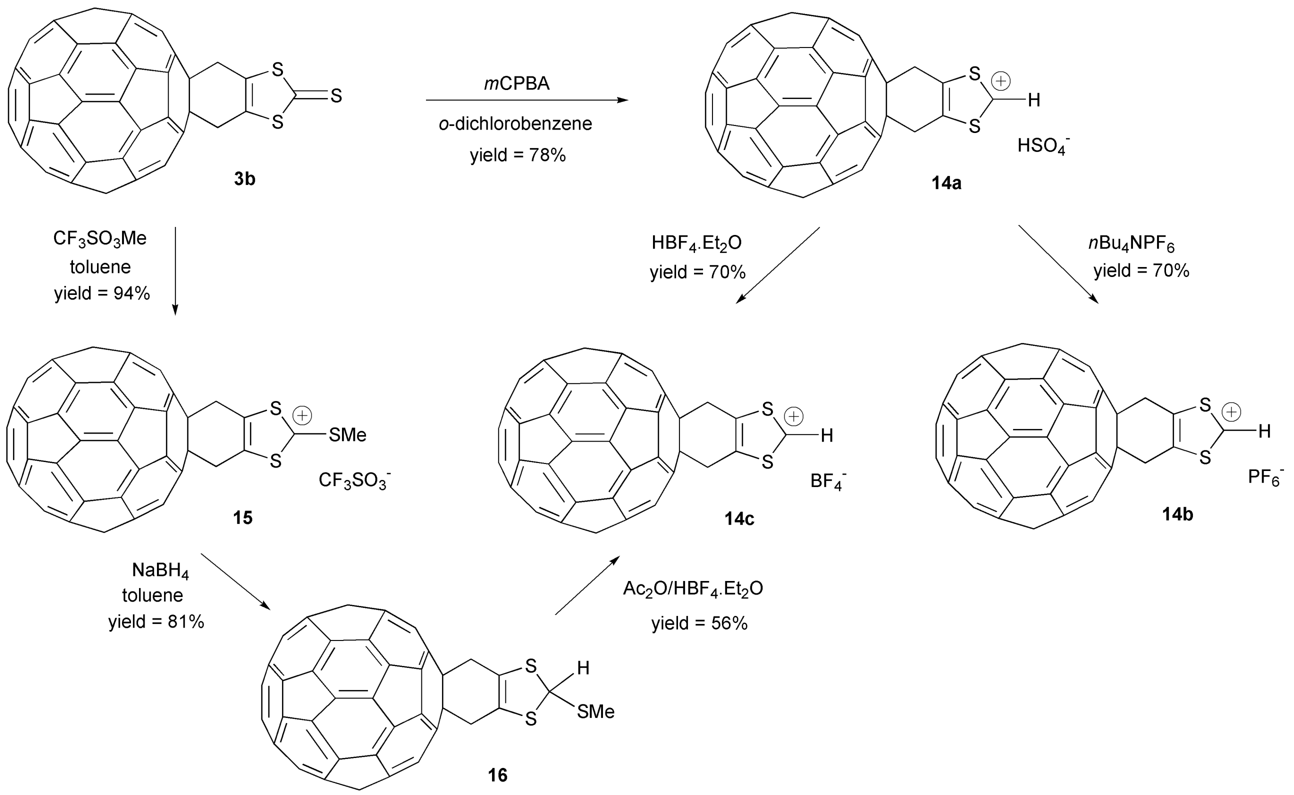
Synthesis of fused 1,3-dithiolium–C_{60} salts

After these different failures in coupling reactions, we considered the alternative route which consisted in the classical carbenoid coupling reaction from 1,3-dithiolium salts to create the TTF core.[52] 1,3-dithiolium–C_{60} salt **14a** was prepared by oxidation with a solution of *m*-chloroperoxybenzoic acid, the surprising presence of the hydrogenosulfate as counterion being in agreement with previous observations on such a reaction (Scheme 11).[53] The anion metathesis was efficiently realized by using tetrabutylammonium hexafluorophosphate or tetrafluoroboric acid to afford 1,3-dithiolium salts **14b** and **14c** respectively. We could also reach the latter compound using a classical multistep pathway well known in TTF chemistry. Starting from **3b**, the 1,3-dithiolium salt **15** was first produced by methylation with methyl triflate in excellent yield. Reduction of **15** with sodium borohydride in toluene was followed by dethiomethylation with tetrafluoroboric acid in acetic anhydride to produce 1,3-dithiolium tetrafluoroborate **14c** in 45% yield for these last two steps.

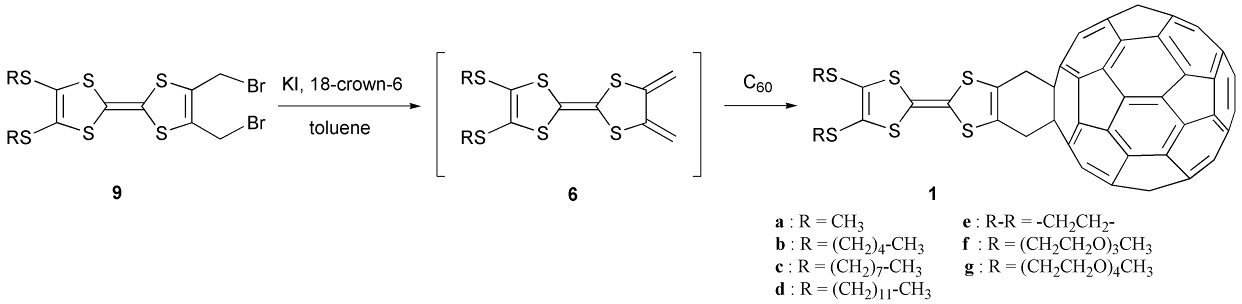
Unfortunately, all our efforts to convert these 1,3-dithiolium compounds into dumbbell **2** upon deprotonation with bases



Scheme 10 Synthesis of 2-oxo(or thioxo or selenoxo)-1,3-dithiole-C_{60} adducts.



Scheme 11 Synthesis of 1,3-dithiolium–C_{60} salts.



Scheme 12 Synthesis of TTF–C_{60} dyads from intermediates 2,3-bis(bromomethyl)TTF.

and carbenoid coupling, according to Scheme 7, were unsuccessful as was the possible conversion into dissymmetrical TTF by using this methodology in the presence of other appropriate 1,3-dithiolium salts.

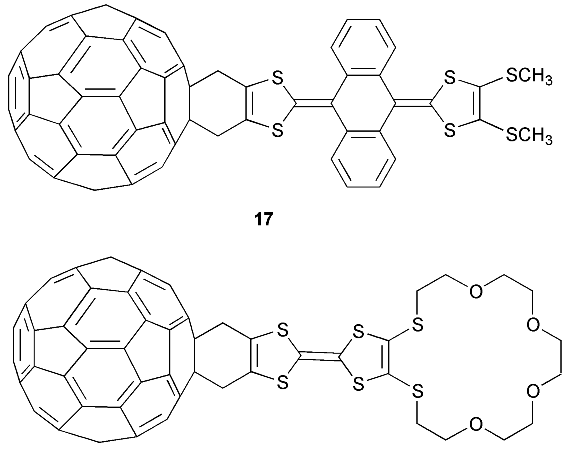
Synthesis of TTF–C_{60} dyads and (TTF)$_n$–C_{60} polyads

Since our first strategy involving the [4 + 2] Diels–Alder cycloaddition of C_{60} and 2-oxo-(or 2-thioxo or 2-selenoxo)-4,5-bis(methylidene)-1,3-dithioles **3** was hindered in the final coupling reaction, we decided to apply an analogous methodology but with prior introduction of the TTF core, *i.e.* by Diels–Alder reaction of transient 2,3-bis(methylidene)–TTF **6** with C_{60} (Scheme 12).[54]

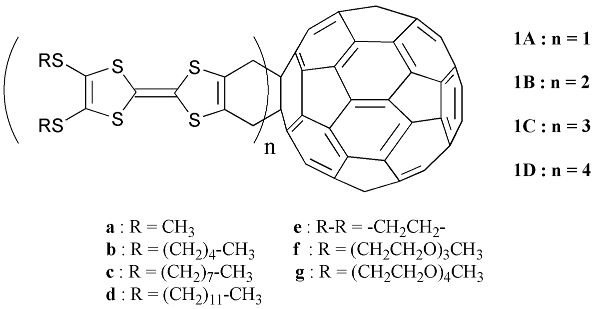
Note that our strategy has been recently used by other groups to introduce either the analogous (π-extended)TTF or a crown ether substituting the TTF core to reach dyads **17**[55] and **18**[56] respectively (Scheme 13).

First, to get the conjugated diene **6**, we decided to use a new class of TTF bearing two vicinal bromomethyl groups. The latter series could be conveniently reached upon treatment of the corresponding 2,3-bis(hydroxymethyl)-6,7-bis(methylsulfanyl)-TTF[57] with phosphorus tribromide (70% yield after silica gel column chromatography).[58] The [4 + 2] cycloaddition of **6** to C_{60} could readily be achieved by treatment of **9** with potassium iodide in the presence of 18-crown-6 and [60]fullerene.[54]

Reaction proceeded to give monoadduct **1A** as the major product (30 to 50% yield), although a mixture of regioisomeric



Scheme 13 Recent applications using this methodology of synthesis.



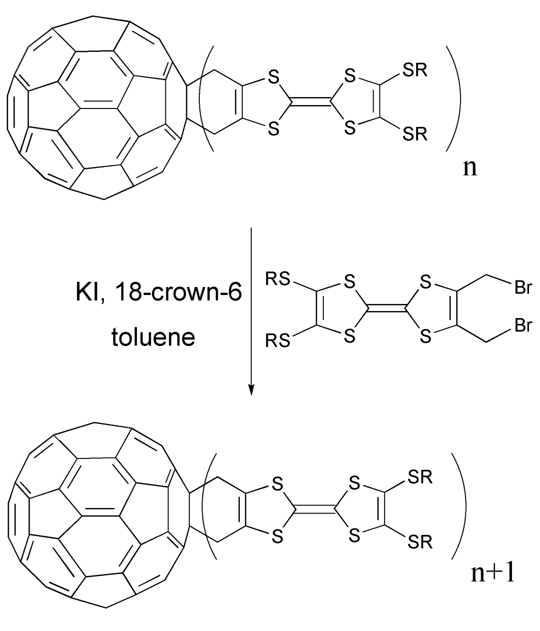
Scheme 14 Efficient route to TTF–C_{60} polyads using a methodology by increment.

diadducts was also obtained in 10–20% yield. Various substituents were introduced on the TTF unit, especially polyalkyloxysulfanyl groups with the aim of increasing the solubility properties of dyads for physical studies and possible applications.

Then we were interested in synthesizing and isolating new diadducts **1B** and unprecedented tri and tetraadducts **1C** and **1D** respectively to provide access to three-dimensional functionalized fullerenes presenting several electroactive units (Scheme 14). Such polyadducts comprised of several isomers resulting from reaction at the different positions on C_{60} could also present a great potentiality of applications.[4a]

These polyads are formed in very low yields by treating 2,3-bis(bromomethyl)TTF **9** with naked iodide in the presence of C_{60}. Consequently, in order to optimize their selective synthesis, we considered their obtention in much higher yields by successive similar treatments of the major adducts produced at each step.[59] Starting from monoadducts **1A**, the subsequent cycloaddition of **1A** with diene **6** was responsible for the formation of diadducts **1B**. Secondly, applying the same methodology by starting from **1B**, we could reach and isolate the desired triadducts **1C** and tetraadducts **1D** in acceptable yields (Scheme 15).[59]

All compounds **1A–D** were separated by column chromatography, but the isolation of polyadducts appeared to be highly dependent on the chromatographic conditions: first, some of these polyadducts appeared not to be stable in chlorinated solvents, except in the case where the TTF core is bearing polyethersulfanyl groups. Secondly, due to the poor solubility of some adducts, we used mixtures of solvents (carbon disulfide, dichloromethane or toluene) as eluent. Finally, to prevent any protic oxidation at the TTF moiety[60] and hence the rapid degradation of some adducts, the eluent was alkalized by the addition of 1% triethylamine. Polyads **1B–D** were obtained as a mixture of numerous regioisomers. Whereas the eight isomers of **1Bb** could be analytically separated by HPLC (Fig. 1 and 2), the chromatographic analysis of the high number of isomers for **1C** and **1D** has not yet been achieved owing to the complexity of the problem.



Scheme 15 $(TTF)_n$–C_{60} polyads structures.

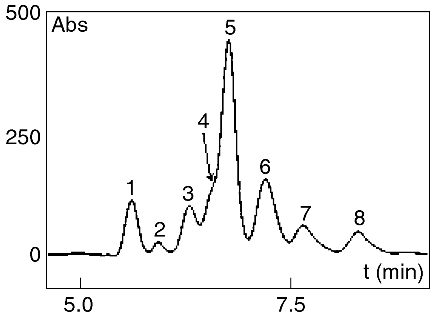


Fig. 1 HPLC separation of regioisomers of **1Bb**.[59] Chromatographic conditions of separation: Shimadzu SCL-10A VP HPLC apparatus; reversed phase KROMASIL 100 analytical column; toluene/CH_3CN (40 : 60) as eluent; flow rate: 0.5 ml min^{-1}; UV detection at 254 nm. Reprinted from D. Kreher, S.-G. Liu, M. Cariou, P. Hudhomme, A. Gorgues, M. Mas, J. Veciana and C. Rovira, *Tetrahedron Lett.*, 2001, **42**, 3447, Copyright 2001, with permission from Elsevier Science.

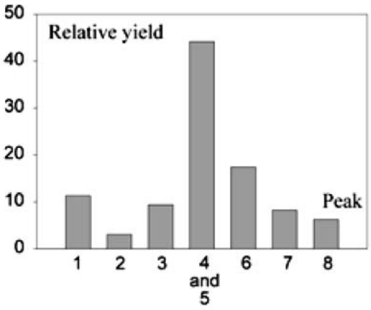


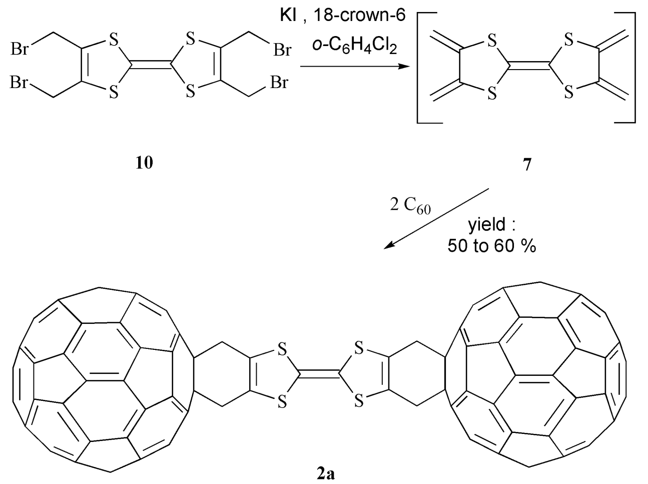
Fig. 2 Relative yields of regioisomers of **1Bb**.[59] Reprinted from D. Kreher, S.-G. Liu, M. Cariou, P. Hudhomme, A. Gorgues, M. Mas, J. Veciana and C. Rovira, *Tetrahedron Lett.*, 2001, **42**, 3447, Copyright 2001, with permission from Elsevier Science.

To our knowledge, the first isolation and characterization of two then four regioisomers of a triad C_{60}–$(TTF)_2$ in which the TTF is bearing methoxycarbonyl groups ($R = CO_2Me$, Scheme 6) was recently achieved by combination of HPLC, UV-Vis spectroscopy and HMBC NMR.[61] In this diadduct, obtained using the Barcelona's route, the *trans-3* and the *equatorial* regioisomers were formed in a comparable relative yield. Similar work was also carried out on the C_{60}–4,5-dimethoxy-*o*-quinodimethane diadduct.[62] By comparison with these previous examples, it seems reasonable for the diadduct **1Bb** to assign the major peak (peak 5) to the *equatorial* regioisomer (Fig. 1).

Synthesis of C_{60}–TTF–C_{60} dumbbell triads

For the synthesis of dumbbell **2a**,[63] a similar strategy was applied (Scheme 16). Tetrakis(hydroxymethyl)TTF[48] was first converted into the corresponding tetrakis(bromomethyl)TTF[58] **10** with phosphorus tribromide in tetrahydrofuran (yield = 70%) and the latter was submitted to a reductive elimination into tetramethylidene[*4H*]TTF **7** with naked iodide in the presence of C_{60}.

Best results were obtained by carrying out the reaction under inert atmosphere, at room temperature, in the dark and in *o*-dichlorobenzene as the solvent. The resulting black precipitate incorporating **2a** was filtered off, ground and washed



Scheme 16 Synthesis of the first C_{60}–TTF–C_{60} dumbbell.

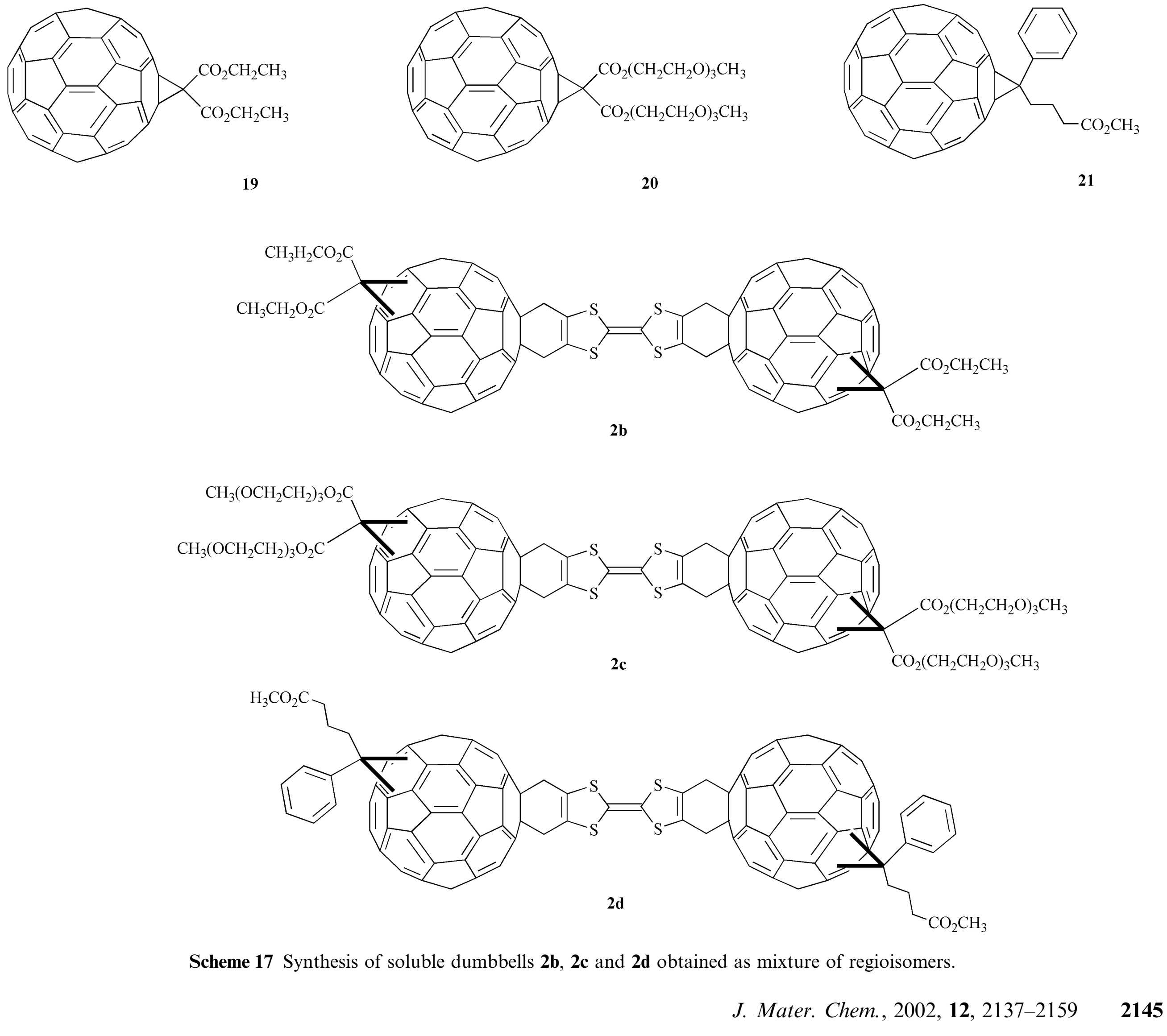
several times, consecutively with carbon disulfide (to remove unreacted C_{60}), an aqueous solution of sodium thiosulfate (to get rid of iodine generated in the reaction), water, acetone, methanol and dichloromethane in order to eliminate all other impurities formed. A second crop of black solid **2a** could be recovered by diluting the *o*-dichlorobenzene solution with dichloromethane (overall yield = 50–60%). Due to its poor solubility and its thermal instability (*e.g. retro* Diels–Alder reaction), we were unable to further purify **2a** by recrystallization, Soxhlet extraction, column chromatography or HPLC.[63]

In order to perform further photophysical studies of such assemblies, we had to solve the problems resulting from the poor solubility of dumbbell **2a**. Thus, we have developed the original synthesis of different dumbbells which present interesting solubility properties in various organic solvents.

To reach analogous dumbbells **2b**, **2c** and **2d** (Scheme 17), the same methodology was applied by replacing C_{60} by the methanofullerene derivatives **19**, **20** and **21** respectively.

Compounds **19** and **20** were synthesized using the [2 + 2] cycloaddition according to the Bingel cyclopropanation of C_{60}.[64] Thus, the treatment of diethyl bromomalonate with sodium hydride in toluene in the presence of C_{60} afforded compound **19** in 58% yield. The methanofullerene **20** substituted with polyalkoxy ester functionalities was obtained in 46% yield by [2 + 2] cycloaddition of di(3,6,9-trioxadecyl) malonate with C_{60} in the presence of both carbon tetrabromide and 1,8-diazabicyclo[3.4.0]undec-7-ene (DBU). In the second step, dumbbells **2b** and **2c** were successfully prepared in 31 and 20% yield respectively by a double [4 + 2] cycloaddition of these methanofullerene derivatives **19** and **20** with the precedent bis-diene **7**.

The synthesis of methanofullerene **21** was carried out following a reported cycloaddition reaction of a diazo compound with C_{60}.[65] In the present case, the diazo compound was generated *in situ* from the *p*-tosylhydrazone derivative (prepared in quantitative yield from ethyl 4-benzoylbutyrate and *p*-toluenesulfonyl hydrazide) by treatment with sodium methoxide in pyridine. The subsequent reaction with C_{60} in *o*-dichlorobenzene at 70 °C afforded the [5,6] isomer which was



Scheme 17 Synthesis of soluble dumbbells **2b**, **2c** and **2d** obtained as mixture of regioisomers.

converted into the [6,6]-methanofullerene in refluxing o-dichlorobenzene. The double [4 + 2] cycloaddition involving diene **7** and methanofullerene **21** afforded dumbbell **2d** in 10% yield. Efforts are now in progress to improve this access to soluble dumbbells in terms of purification and yield.

Molecular orbital calculations

The optimized structure of C_{60}–TTF–C_{60} **2** was calculated with the PM-3 method[66] and showed that the cyclohexene ring adopts in the ground state a boat conformation as previously shown for other Diels–Alder cycloadducts of C_{60}.[21b,42b,67] The molecular orbital energies and electron densities were calculated using GAUSSIAN 98 (HF/3–21G level)[68] with the following results : for the *trans*-form, LUMO (-1.496 eV) and HOMO (-6.755 eV) and for the *cis*-form, LUMO (-1.332 eV) and HOMO (-6.710 eV). As expected, the electron densities of the HOMO is predominantly localized onto the TTF moiety, while the LUMO is localized onto C_{60}. The heat of formation of the *trans*-form (7460 kJ mol^{-1}) is lower than that of the *cis*-form (7820 kJ mol^{-1}), suggesting that the *trans*-form is more stable. The distances between the centre of TTF and the centre of one of the C_{60}-moieties were calculated to be 9.2 Å for the *trans*-form (Fig. 3).

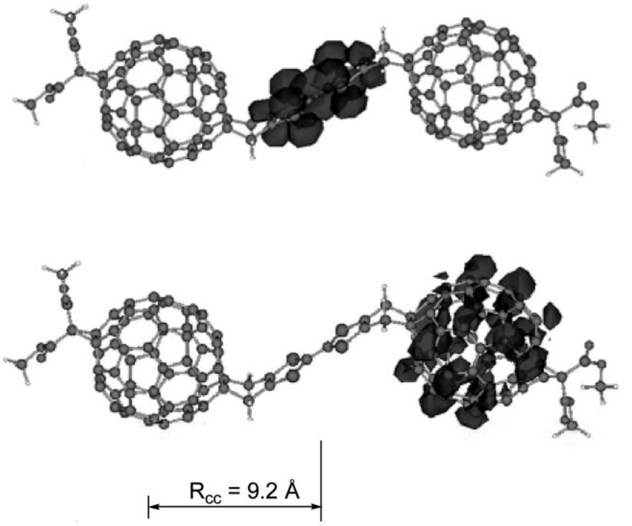


Fig. 3 PM3-optimized geometry of C_{60}–TTF–C_{60} dumbbell (substituted by methanofullerenes with methoxycarbonyl groups) and HOMO (top)/LUMO (bottom) orbitals calculated by GAUSSIAN 98 (HF/3-21G level).

We should note that the calculated distance between the sulfur atom of the TTF core and the nearest sp^2 carbon atom of C_{60} was estimated to be 4.1 Å which is not so far from the sum of the van der Waals radii of both atoms (3.5 Å) (Fig. 4).[69] This value has to be compared with those reported for molecules **III** (4.8 Å), **I** with $n = 1$ (7.6 Å) or with $n = 2$ (10.5 Å), assuming a fixed conformation.[26]

This result is in agreement with the concept which motivated this current work, *i.e. i*) controlling the rigidification between both donor and acceptor units, *ii*) maintaining a short distance between these two units.

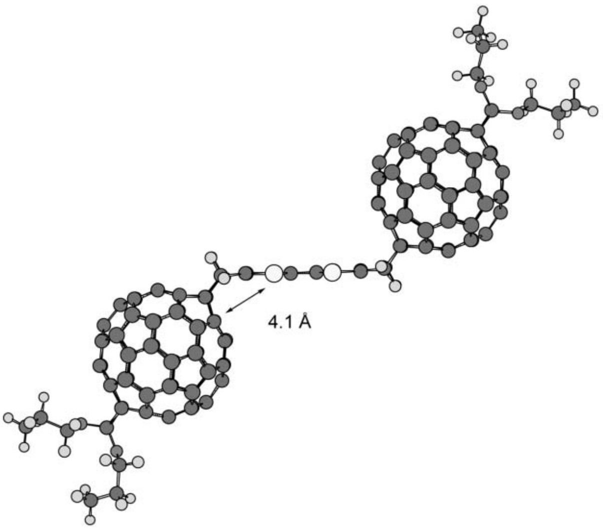


Fig. 4 Shortest distance between the sulfur atom of the TTF core and the nearest carbon atom of C_{60}.

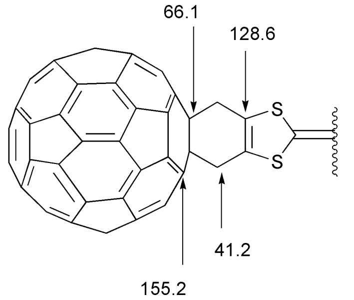
Spectroscopic characterizations

The structures of these different Diels–Alder adducts were confirmed by their analytical and spectroscopic data.

NMR spectroscopy

Concerning 2-oxo(or 2-thioxo or 2-selenoxo)-1,3-dithiole-C_{60} systems **3**, dyads and polyads **1**, the chemical shift in ^1H NMR of the methylenic group of the cyclohexene ring appeared to be smoothly dependent on the substitution (*ca.* 4.3 ppm). The ^{13}C chemical shifts of the principal carbon atoms are given in Scheme 18 in the case of dyad **1Ab**.

Despite many efforts devoted to the characterization of dumbbell **2a**, in its ^1H NMR spectrum (500 MHz, o-$C_6D_4Cl_2$), the expected singlet at about 4.2–4.3 ppm corresponding to the CH_2 bridges has not been evidenced. We could attribute this phenomenon to: *i*) either the very weak solubility of **2a**, *ii*) or the possible bad relaxation of the methylene protons because of their proximity to C_{60} (although this is not the case in the corresponding monoadducts and polyadducts **1**), *iii*) or the presence of paramagnetic species in compound **2a** giving rise to a contact shift arising at very low concentration and in condition of fast exchange.[60]



Scheme 18 ^{13}C chemical shifts of the principal carbon atoms of dyad **1Ab**.

Mass spectrometry

Dyads and polyads **1** were characterized by mass spectrometry, using the MALDI-TOF technique in positive or negative mode with different matrix and solvent combinations (9-nitroanthracene–toluene or 9,10-dimethylanthracene–dichloromethane or dithranol–dichloromethane).

Indeed, most of these compounds exhibited the molecular ion peak with the expected isotopic distribution. Moreover, the mass spectrum of these (poly)adducts showed the peaks corresponding to the successive *retro* Diels–Alder fragmentations and/or the well known fragmentation of the TTF central double bond.[70]

For dumbbell **2a**, using the MALDI-TOF technique (with 9,10-dimethylanthracene as the matrix), peaks at $m/z = 256$ and at $m/z = 720$ are observed. These fragments unambiguously agree with the *retro* Diels–Alder fragmentation of dumbbell **2a** respectively into bis-diene **7** and C_{60}. Moreover,

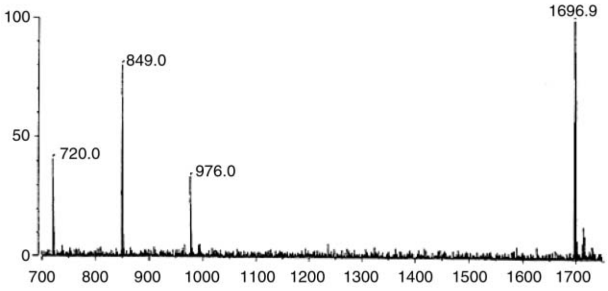


Fig. 5 Low-resolutionpositive-ion electrospray mass spectra of dumbbell **2a** recorded at 300 V by means of magnetic field linear scans.[71] Reproduced with permission from D. Rondeau, D. Kreher, M. Cariou, P. Hudhomme, A. Gorgues and P. Richomme, *Rapid Commun. Mass Spectrom.*, 2001, **15**, 1708, Copyright 2001, ©John Wiley & Sons Limited.

the mass spectrum exhibited another peak at *m*/*z* = 847 (M/2 − 1) corresponding to the fragmentation of the TTF central double bond. By using dithranol (1,8-dihydroxy-9(10*H*)-anthracenone) as the matrix, we finally succeeded in clearly evidencing the molecular peak at *m*/*z* = 1696 with the expected isotopic distribution (Fig. 5), and the peak at *m*/*z* = 976 corresponding to the mono *retro* Diels–Alder fragmentation.[63] For dumbbells **2b–d**, using the MALDI-TOF technique, mass spectra exhibited the peak at *m*/*z* = M/2 − 1 which was attributed to the TTF central bond fragmentation and peaks corresponding to the *retro* Diels–Alder fragments.

Dumbbells **2a** and **2b** were also studied by the electrospray technique as a good alternative to MALDI-TOF experiments.[71] Thus, the high-resolution mass spectrum of **2a** showed also a mass-to-charge ratio and an isotopic distribution in the molecular peak which correspond to the expected values for the radical cation of **2a** in the positive-ion mode.

It was also clearly shown that the mass spectrum of **2a** could be obtained essentially free of dissociation using optimized experimental parameters. In particular, by increasing the molecular ion internal energy, the mass spectrum exhibited more intensive fragment ion peaks (Fig. 5).

Corresponding peaks at *m*/*z* 720 and 976 should be the result of the *retro* Diels–Alder fragmentation (Scheme 19). The peak of the ion at *m*/*z* 849 was more surprising, but accurate mass measurements confirmed its elemental composition $[C_{65}H_5S_2]^+$. This could suggest a long-distance hydrogen migration to the TTF central double bond, followed by an *i*-cleavage, as previously proposed for halotetrathiafulvalenes in electron ionization mass spectrum.[72]

On high-resolution spectra of other dumbbells **2b–d**, using the electrospray technique in positive-ion mode, molecular peaks of the corresponding radical cations, and their molecular mass determined exactly, were observed.

UV-Visible spectroscopy

In the visible region, the spectra of all C_{60}-based cycloadducts showed a weak and sharp absorption band around 435 nm and a weak absorption band at 700 nm. The latter is consistent with an adduct of C_{60} at the more reactive [6,6]-ring junction with a closed transannular bond.[73] In the UV-Vis spectrum of TTF–C_{60} dyads **1**, as well as for dumbbells **2**, a weak broad absorption band between 450 and 530 nm is present which was previously ascribed to weak electronic interactions between donor and acceptor moieties (Fig. 6).[42b] However, no intermolecular charge transfer band could be detected between 900 and 3000 nm.

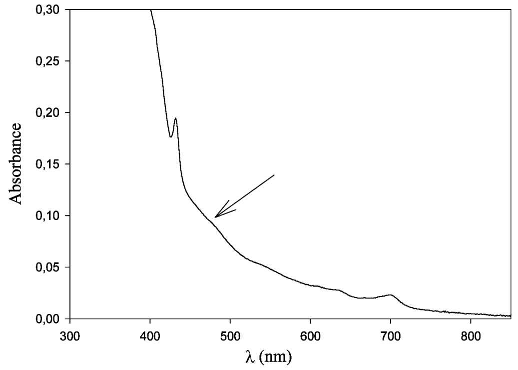
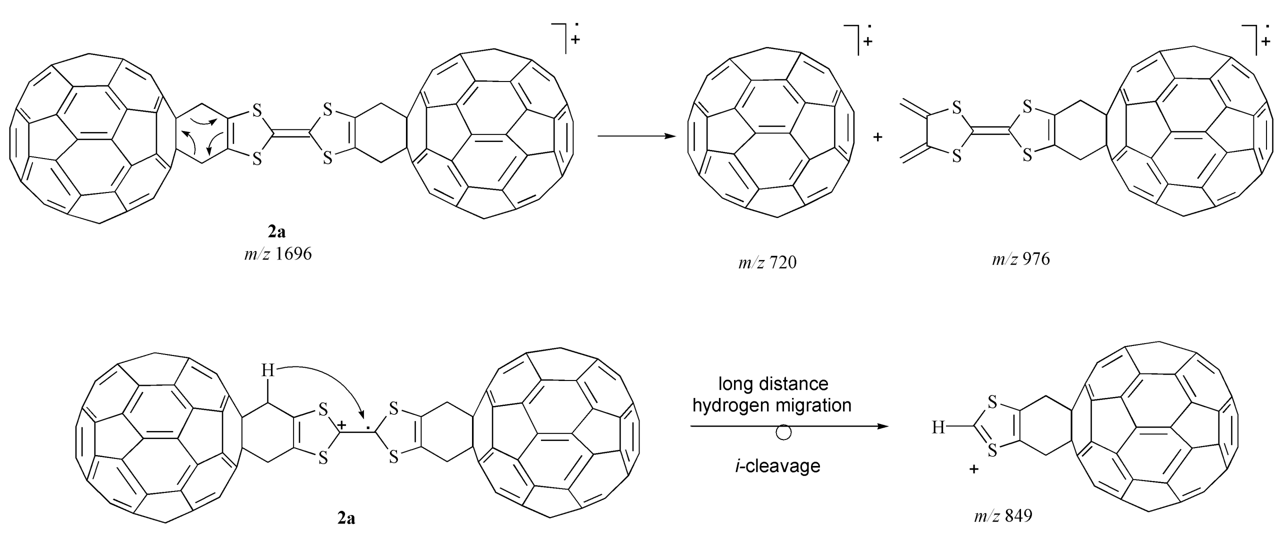


Fig. 6 UV-Visible spectrum of TTF–C_{60} dyad **1Ab** in *o*-dichlorobenzene.

The optical properties of the radical cations and dications of TTF–C_{60} dyads, $(TTF)_n$–C_{60} polyads and C_{60}–TTF–C_{60} dumbbells were investigated by UV-Visible and near-IR spectroscopies, by addition of increasing amounts of nitrosonium tetrafluoroborate ($NOBF_4$) in dichloromethane or toluene at room temperature. Chemical oxidation led to the rapid disappearance of neutral TTF derivative and to the development of new bands characteristic of the radical cation (centered on 450 nm and 760 nm) (Fig. 7) then of the dication (centered on 335 nm) (not shown).[74] Polyads **1B** and **1C** presented the same behaviour as monoadducts **1A** (Fig. 8).

This chemical oxidation was also carried out on dumbbells **2b–d** by addition of increasing amounts of $NOBF_4$ in dichloromethane. Characteristic bands of the radical cation (centered on 470 nm and 660 nm), then of the dication (centered on 330 nm) were evidenced for these different assemblies.



Scheme 19 Proposed structures for the *m*/*z* 849 and 976 peaks.

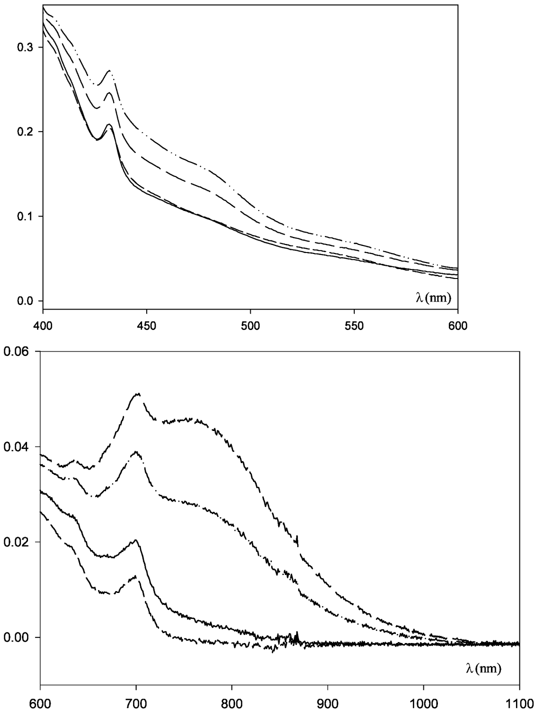


Fig. 7 Transformation of the UV-Visible spectrum of TTF–C_{60} dyad **1Ah** during chemical oxidation (Conc. = 10^{-4} M in CH_2Cl_2, l = 1 mm).

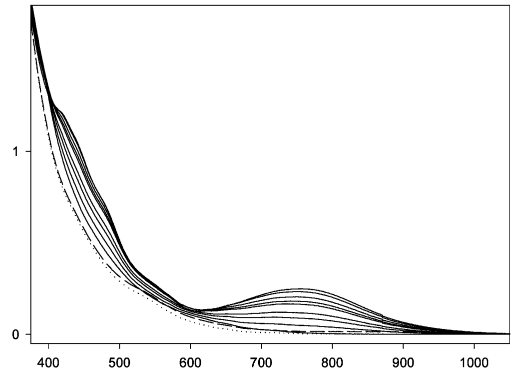


Fig. 8 Transformation of the UV-Visible spectrum of $(TTF)_2$–C_{60} triad **1Bh** during chemical oxidation (Conc. = 10^{-4} M in CH_2Cl_2, l = 10 mm).

Electrochemical properties

Cyclic voltammetry. In cyclic voltammetry, cycloadducts **1A–D** show two reversible oxidation peaks, corresponding to the radical cation and dication states of the TTF moiety, and one to four quasi-reversible reduction peaks, due to the reduction steps of the fullerene moiety (Fig. 9). These reduction potentials are shifted to more negative values when compared to those of pristine C_{60}, this corresponding to the classical behaviour of fullerene derivatives and the successive saturation of [6,6] double bonds of C_{60} (table 1).[75] It should be noted that the increasing number of TTF units linked to C_{60} decreases its acceptor character by successive loss of conjugation and grafting of electron-rich TTF groups. Moreover, by difference between the first oxidation and the first reduction processes, we could estimate the corresponding gap at 1.35–1.40 V.

Concerning the polyads **1B–D**, the ratio between the intensities of the first oxidation peak of TTF and the first reduction peak of C_{60} was estimated to be $n \pm 10^{-1}n$ for **1B–D**, from deconvoluted voltammograms (Fig. 10). Since the diffusion coefficient is the same on both reduction and oxidation peaks, this fact confirms that these adducts **1A–D** are made up of one C_{60} acceptor and n TTF donors.

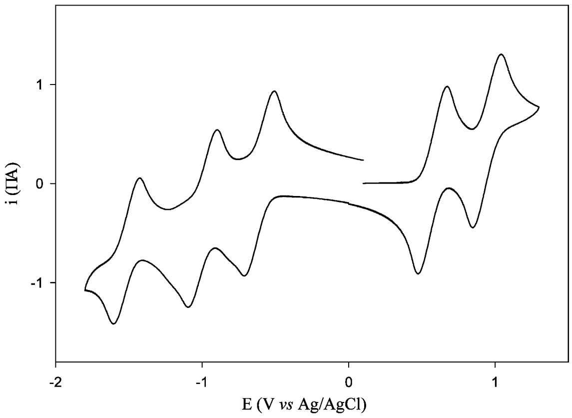


Fig. 9 Cyclic voltammogram of dyad **1Ag**, Conc. ~10^{-3} M in o-$C_6H_4Cl_2$–$n$$Bu_4NPF_6$ 0.05 M; Pt electrode; v = 100 mV s^{-1}.

Table 1 Redox potentials E_{red} and E_{ox} (V *vs* Ag/AgCl) of monoadducts **1A**, diadducts **1B**, triadducts **1C** and tetraadducts **1D**; Conc. ~ 10^{-3}M in o-$C_6H_4Cl_2$–$n$$Bu_4NPF_6$ 0.05 M; Pt electrode; v = 100 mV s^{-1}

	E_{red} 1	E_{red} 2	E_{red} 3	E_{ox} 1	E_{ox} 2
C_{60}	−0.61	−1.00	−1.45	—	—
1Aa	−0.72	−1.11	−1.61	+ 0.64	+ 1.08
1Ba	−0.75	−1.12	−1.84	+ 0.62	+ 1.02
1Ca	−0.77	−1.06	—	+ 0.63	+ 1.05
1Ab	−0.72	−1.09	−1.59	+ 0.65	+ 1.09
1Bb	−0.82	−1.20	−1.83	+ 0.70	+ 1.16
1Cb	−0.98	−1.35	—	+ 0.69	+ 1.14
1Db	−1.16	—	—	+ 0.61	+ 0.84
1Ac	−0.72	−1.08	−1.60	+ 0.64	+ 1.14
1Ad	−0.72	−1.17	—	+ 0.65	+ 1.15
1Ae	−0.71	−1.10	−1.60	+ 0.66	+ 1.16
1Be	−0.85	−1.22	−1.85	+ 0.65	+ 1.09
1Ce	−0.98	−1.35	—	+ 0.72	+ 1.10
1Af	−0.71	−1.09	−1.61	+ 0.67	+ 1.04
1Bf	−0.83	−1.22	−1.85	+ 0.69	+ 1.07
1Cf	−0.96	−1.34	—	+ 0.72	+ 1.11
1Df	−1.16	—	—	+ 0.73	+ 1.13
1Ag	−0.71	−1.08	−1.60	+ 0.68	+ 1.05
1Bg	−0.85	−1.24	−1.61	+ 0.68	+ 1.03
1Cg	−0.95	−1.38	−1.67	+ 0.73	+ 1.08

In o-dichlorobenzene, the cyclic voltammogram of dumbbell **2a** exhibited two reversible oxidation peaks, corresponding to the radical cation and dication states of the TTF moiety, at +0.56 and +1.09 V respectively and three reversible or quasi-reversible reduction peaks, corresponding to the reduction steps

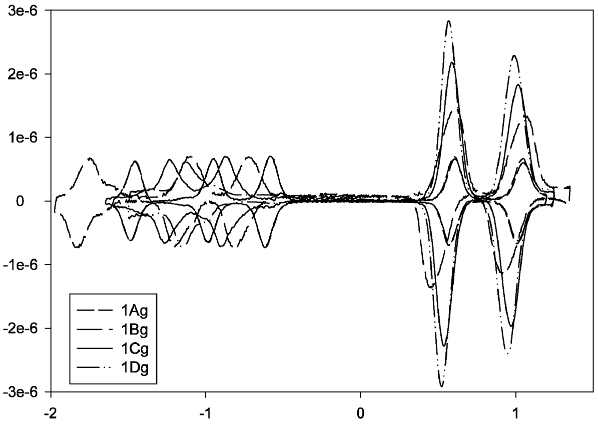


Fig. 10 Deconvoluted cyclic voltammograms of polyads **1A–Dg**, Conc. ~ 10^{-3} M in o-$C_6H_4Cl_2$–$n$$Bu_4NPF_6$ 0.05 M; Pt electrode; v = 100 mV s^{-1}.[59] Reprinted from D. Kreher, S.-G. Liu, M. Cariou, P. Hudhomme, A. Gorgues, M. Mas, J. Veciana and C. Rovira, *Tetrahedron Lett.*, 2001, **42**, 3447, Copyright 2001, with permission from Elsevier Science.

Table 2 Redox potentials E_{red} and E_{ox} (V *vs* Ag/AgCl) of dumbbells **2a–d**; Conc. ~ 10^{-3}M in o-$C_6H_4Cl_2$–$n$$Bu_4NPF_6$ 0.05 M; Pt electrode; v = 100 mV s^{-1}

	E_{red} ^{1}	E_{red} ^{2}	E_{red} ^{3}	E_{red} ^{4}	E_{ox} ^{1}	E_{ox} ^{2}
C_{60}	−0.61	−1.00	−1.45	−2.08	—	—
2a	−0.66	−1.02	−1.55	—	+ 0.56	+ 1.09
2b	−0.78	−1.34	−1.60	—	+ 0.58	+ 1.11
2c	−0.88	−1.13	−1.65	—	+ 0.62	+ 1.04
2d	−0.81	−1.19	—	—	+ 0.61	+ 1.10

of the fullerene moiety at −0.66, −1.02 and −1.55 V (*vs* Ag/AgCl) (Table 2).[63] The ratio between the intensity of the C_{60} first reduction peak and the intensity of the TTF first oxidation peak was estimated to be 2.0 ± 0.1 from experimental and deconvoluted voltammograms at several scan rates. Since the diffusion coefficient is the same on both reduction and oxidation peaks, this confirms that dumbbell **2a** is made up of two C_{60} acceptor moieties and one TTF donor core. We could also estimate the gap (1.22 V) by difference between the first oxidation and the first reduction processes.

The shift to more negative values reduction potentials for dumbbells **2b–d** compared to those of **2a** is in agreement with the second substitution of C_{60} *via* the cyclopropanation and the subsequent loss of conjugation of C_{60}.

EPR spectroscopy. Our first studies on TTF–C_{60} dyad **1A** clearly showed in the EPR spectrum, both in the solid state and in solution (Fig. 11), the presence of electronic spins which were estimated to represent about 1% of radicals in the sample (g = 2.0058).[54] Consequently, further studies were necessary to understand these surprising results and the origin of these signals. Actually, as happens with pristine C_{60},[76] this EPR signal showed a reversible oxygen-dependent spin concentration although its intensity is one order of magnitude higher than that of C_{60}. Consequently, these radical species could not be ascribed to an intramolecular electron transfer process. This suggested that an extrinsic oxidation has occurred, resulting from : *i*) the purification step (chromatography on silica gel), *ii*) either the solvent, *i.e.* protic doping of the TTF moiety in these two cases,[60] *iii*) or doping in the presence of residual oxygen.

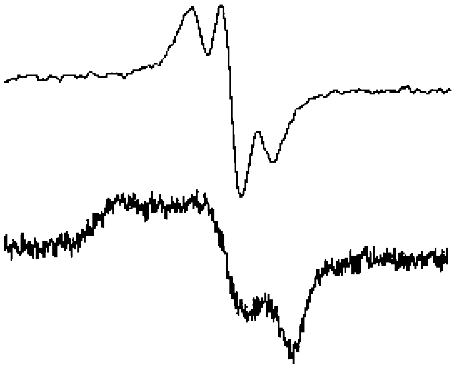


Fig. 11 EPR spectra of TTF–C_{60} dyad **1Ab** in an o-dichlorobenzene solution (top) and in the solid state (bottom).

The presence in the same molecule of electron donor and acceptor made possible the generation of their radical cation and radical anion species upon oxidation or reduction respectively (Scheme 20).

Thus, the mono-radical cation of monoadduct **1Af** was generated by electrochemical oxidation and monitored by EPR spectroscopy (Fig. 12a) (Table 3). An EPR signal related to the radical cation was observed, this appearing as a triplet resulting from the coupling of the single electron on the TTF core with two axial protons of both methylene bridges. This result was previously related to the rigid boat conformation adopted by

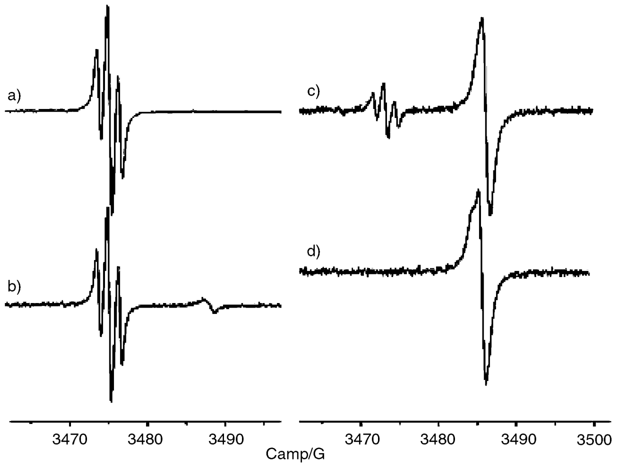
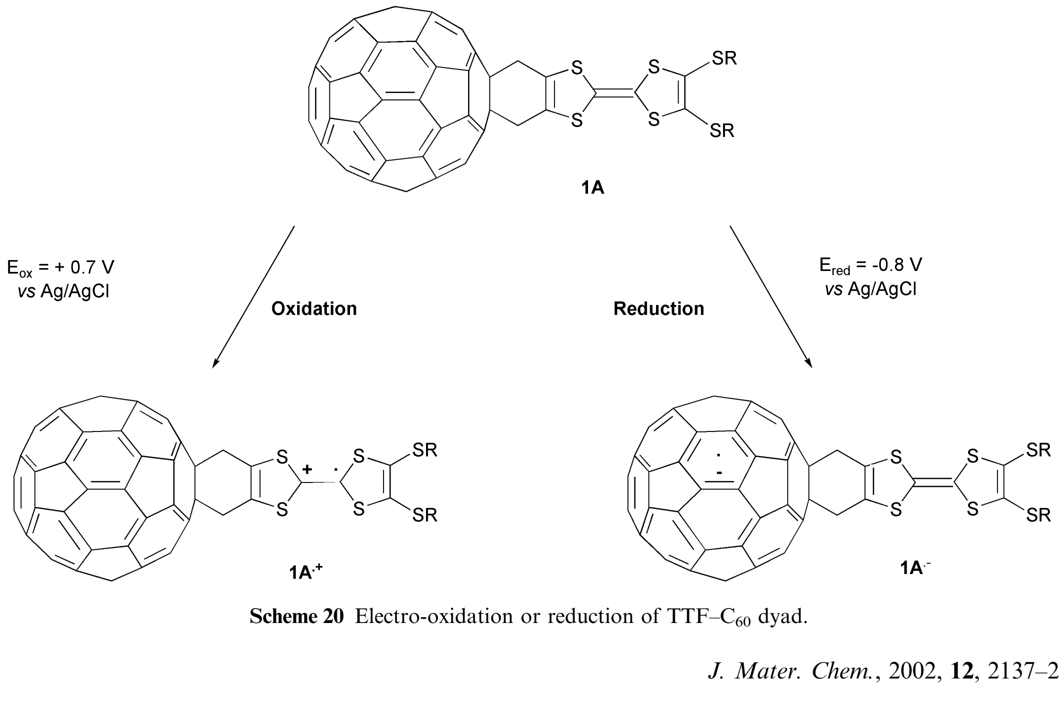


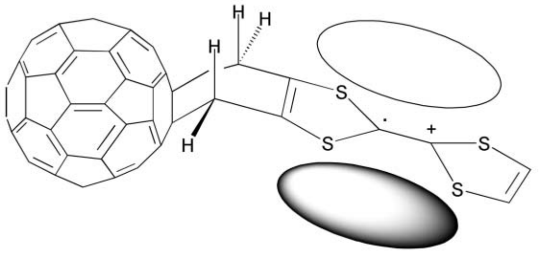
Fig. 12 EPR signature of radical cation of dyad **1Ae** obtained by electrooxidation (for a); upon electroreduction, after 6 min (for b), 16 min (for c) and 25 min (for d), signature corresponding to the formation of the radical anion. Lifetimes of these radical species were estimated of the order of days.



Scheme 20 Electro-oxidation or reduction of TTF–C_{60} dyad.

Table 3 EPR data of radical cation and radical anion species from monoadducts **1Aa–g** and bis-adduct **1Be** (electrochemical experiments carried out in *o*-dichlorobenzene* or dichloromethane**) for the monoradical^{a} or biradical^{b}

	Radical cation				Radical anion	
	g	a_H (G)	a_S (G)	ΔH_{pp} (G)	g	ΔH_{pp} (G)
C_{60}*	—	—	—	—	1.9998	1.02
1Aa**	2.0075	1.45	3.96	0.65	1.9998	1.62
1Ab*	2.0075	1.45	4.00	0.85	2.0000	1.21
1Ac**	2.0076	1.37	3.98	0.90	1.9999	0.98
1Ad**	2.0073	1.43	3.98	0.95	1.9999	0.95
1Ae*	2.0071	1.39	3.80	0.50	1.9997	1.08
1Af**	2.0074	1.44	4.06	0.70	1.9998	1.54
1Ag**	2.0074	1.44	4.04	0.75	1.9998	1.48
1Be	2.0070	1.41^{a}0.76^{b}	—	0.45	2.0002	0.90



Scheme 21 Representation of methylenic hydrogen atoms that explains the coupling of the electronic spin with the two axial hydrogen atoms of the cyclohexene ring.

the cyclohexene ring. Effectively, as shown in Scheme 21, equatorial hydrogen atoms are essentially lying in the plane of the TTF ring where the spin density is null. Additional satellite lines, derived from the ^{33}S hyperfine coupling constant are also observed indicating that the electronic spin is mainly localized on the carbon of the central bond of the TTF core. The observed g values and coupling constants are in agreement with those previously reported on such systems or for radical cations of TTF derivatives.[77]

By imposing a reduction potential at −0.8 V *vs* Ag/AgCl, we could observe the slow disappearance of the signal corresponding to the radical cation and the appearance of the signal of the radical anion. The signal related to this radical anion was characterized as a large singlet line, suggesting that the spin density distribution is confined and delocalized on the fullerene cage.

Concerning bis-adducts, EPR studies of the isomeric mixture of triad **1Be** gave very similar results as those obtained for the C_{60}–TTF_2 bearing methoxycarbonyl groups (R = CO_2Me, Scheme 6)[61b] Upon oxidation the monoradical-cation is formed first, and then the biradical-cation starts to appear. Fig. 13 shows the EPR spectrum obtained upon oxidation during 30 min of compound **1Be**. The spectrum correspond to the sum, in a 3 : 4 proportion, of the monoradical and biradical at the fast exchange limit. Electroreduction gave the corresponding radical anion at g = 2.0002.

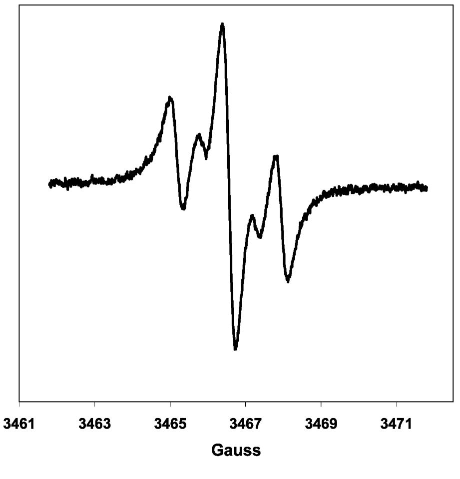


Fig. 13 EPR spectrum at 293 K in CH_2Cl_2 under isotropic conditions of the radical cation derived from **1Be** after 30 min of *in situ* electrochemical oxidation.

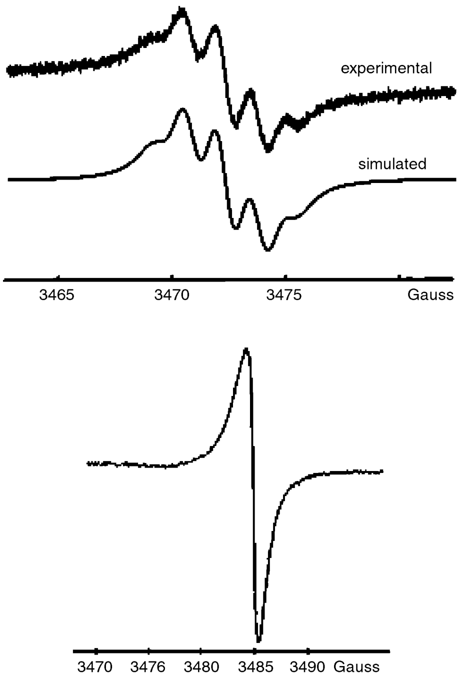


Fig. 14 EPR spectra of **2a** in *o*-$C_6H_4Cl_2$–*n*Bu_4NPF_6 0.05 M, after electrooxidation (top) and electroreduction (bottom) respectively.[63] Reprinted from S.-G. Liu, D. Kreher, P. Hudhomme, E. Levillain, M. Cariou, J. Delaunay, A. Gorgues, J. Vidal-Gancedo, J. Veciana and C. Rovira, *Tetrahedron Lett.*, 2001, **42**, 3717, Copyright 2001, with permission from Elsevier Science.

Similar experiments were carried out on dumbbell **2a** (Fig. 14) and EPR spectroscopy provided detailed information about the electronic structure of the ion radical species derived from this triad. Thus two clear signals corresponding to the cation radical and radical anion were observed upon controlled oxidation and reduction of **2a** respectively (Table 4).

The radical anion EPR signal of **2a**, generated by electroreduction at −0.8 V (*vs* Ag/AgCl), shows the characteristic line (ΔH_{pp} = 1.62 G, g = 1.9998) of fullerides derived from C_{60} cycloadducts (Table 4). On the other hand, the highly persistent cation radical EPR signal obtained by electrooxidation of **2a** at + 0.7 V consists of five overlapped lines with the typical pattern of a coupling with four equivalent protons (g = 2.0073, a_H = 1.40 G and ΔH_{pp} = 1.05 G). Both the g factor and coupling constant with the protons are very similar to those found for the cation radicals derived from related cyclohexene fused C_{60}–TTF dyads.[42b] On these grounds, the four protons can be

Table 4 EPR data of radical cation and radical anion species from dumbbells **2a–d** (electrochemical experiments were carried out in *o*-dichlorobenzene

	Radical cation			Radical anion	
	g	a_H (G)	ΔH_{pp} (G)	g	ΔH_{pp} (G
2a	2.0073	1.40	1.05	1.9998	1.62
2b	2.0072	1.43	1.01	2.0001	1.32
2c	2.0071	1.40	0.96	2.0003	2.90
2d	2.0070	1.41	1.02	2.0002	2.24

assigned to the four equivalent axial methylenic protons of the two cyclohexene bridges expected from the structure of triad **2a**.

Physical properties

Nonlinear optical and optical limiting properties. The research in the area of organic materials for nonlinear optics is motivated by the realization of quantum electronics or electrooptics devices allowing rapid processing and a dense data storage. Materials possessing large nonlinear optical coefficients not only at room temperature are under intensive study in view of the many applications which could be realized with such compounds.[78] Consequently, over the past two decades, considerable interest has been focused on organic compounds with large nonlinear optics coefficients. We should underline here that nonlinear optics can be used also as a tool for diagnosis of physical properties such as low-temperature phase transitions. Thus, we have studied photoinduced optical second harmonic generation (PISHG) and two-photon absorption (TPA) on functionalized fullerenes, such as 2-thioxo-1,3-dithiole-C_{60} **3b** and TTF–C_{60} dyads **1Aa** and **1Ab**.

Photoinduced effects in these compounds are using nonlinear optical techniques. PISHG and TPA measurements were carried out on these cycloadducts in the solid state and in solution.[79] We showed an important role of vibrational and rotational contributions to the PISHG signal in the C_{60}-based compounds studied. The contribution arising from charge distribution asymmetry appeared to be the largest in the fullerene derivatives. Investigations of PISHG *versus* temperature gave the possibility of using PISHG as a sensitive tool for detecting low temperature phase transitions in TTF–C_{60} derivatives.[80] TPA measurements were performed *versus* pressure and time delay between the pump and probe beams (λ = 530 nm) on 2-thioxo-1,3-dithiole-C_{60} cycloadduct **3b**. We showed the existence of TPA in compounds **3b**, **1Aa** and **1Ab** (Fig. 15) and the transmission *versus* time delay was studied in order to control modulation of transmission. The experimental data obtained showed the existence of one maximum of transmission in the range of 0.2 to 0.5 ps. Thus, this fact allowed us to conclude that nonlinear transmission can be modulated. The photoinduced effects (PISHG, TPA) were also studied under applied pressure and temperature *p-T*. Maximum photoinduced changes at 88 K for time delays in the range 0.2 to 0.5 ps were shown.

The essential influence on the observed photoinduced effects was modelized for the different cycloadducts **3b**, **1Aa** and **1Ab**. Based on theoretical model and experimental data concerning PISHG and TPA, it appeared that the length of the chain on the donor TTF greatly influences the behaviour of the pressure-induced changes of nonlinear optical susceptibilities.[79a,c] Using molecular-dynamics simulations and quantum chemical calculations, we showed an asymmetry in the excited configuration interaction (CI) states. Such asymmetry essentially influences the nonlinear optical properties of the modified C_{60} and causes the charge-density redistribution both on the intramolecular as well as on the intermolecular levels. This leads to the increase of nonlinear optical properties of studied compounds.

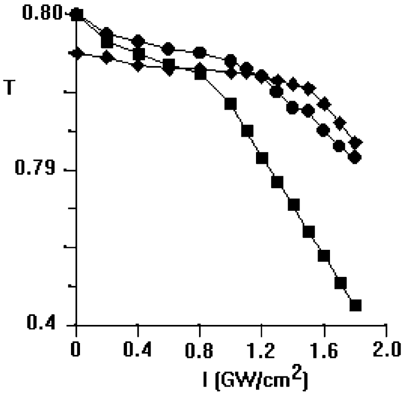


Fig. 15 Transmission *versus* the intensity of the pump beam *I* for **3b** (■); **1Aa** (◆); **1Ab** (●).

On the other hand, we studied the linear electro-optic (LEO Pockels) and nonlinear quadratic electro-optic effects (QEOE Kerr) described by the effective tensor component r_{222} and R_{222} coefficients respectively (Fig. 16). We showed that the R_{222} coefficient (QEOE) was a function of temperature in the case of **3b**. We could also observe the existence of one maximum at about – 60 °C, suggesting the existence of phase transition.

We should notice here that LEO (described by r_{222}) dependencies with the applied pressure–temperature (*p-T*) was observed for the first time in the TTF–C_{60} cycloadducts, as illustrated with the evolution of r_{222} *versus p-T* for C_{60} and compound **1Aa** (Fig. 17 and 18).

Theoretical model and experimental data appeared to be in good agreement. Based on quantum chemical calculations, the results gave unambiguous answers about the role played by electron-vibration interactions (EVIs) in the measured LEO coefficients. A theoretical modeling of the *p-T*-dependent LEO effect was proposed, and the key features of the experimental results were reproduced numerically. A new type of EVI manifestation of multiconformational systems in the LEO phenomenon was shown.[79c] We proved that the induced fluctuations become important for the TTF–C_{60} dyad, because such a system exhibits a delicate balance of the inter-configuration (*p-T*-dependent) states. The LEO effects are unusual among the nonlinear optical ones, which are sensitive to such kinds of phase transitions.

We can conclude that such TTF–C_{60} compounds present large optical limiting properties and they can find interesting applications in optical limitation process.[81] We also showed that soluble TTF–C_{60} based compounds could be a suitable system for optical recording and erasing of holograms under weak laser illumination.

Photophysical properties. In these linked TTF–C_{60} systems, absorption of light by the fullerene moiety leads to the formation of the excited singlet state of fullerene, which rapidly undergoes an intramolecular electron transfer process to form the charge-separated state. This photoinduced electron transfer

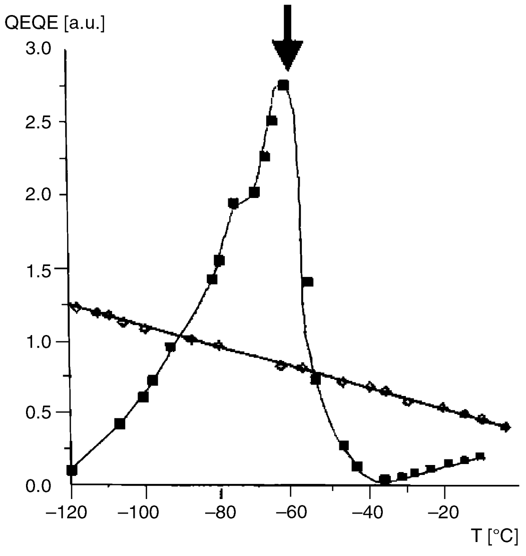


Fig. 16 Calculated dependencies of the effective QEOE tensor component R_{222} *versus* pressure and temperature for pristine C_{60} (●) and for **3b** (■).

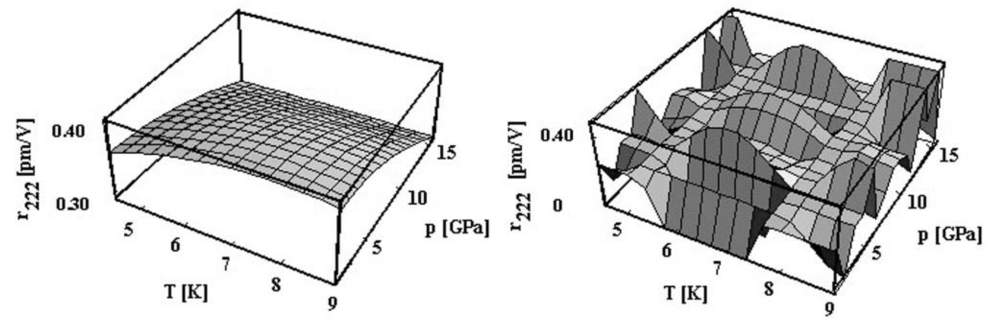


Fig. 17 Calculated dependencies of the effective LEO tensor component r_{222} coefficient *versus* pressure and temperature for C_{60} (left) and dyad **1Aa** (right).[79c] Reprinted (in part) with permission from B. Sahraoui, I. Kityk, P. Hudhomme and A. Gorgues, *J. Phys. Chem. B*, 2001, **105**, 6295, Copyright 2001, American Chemical Society.

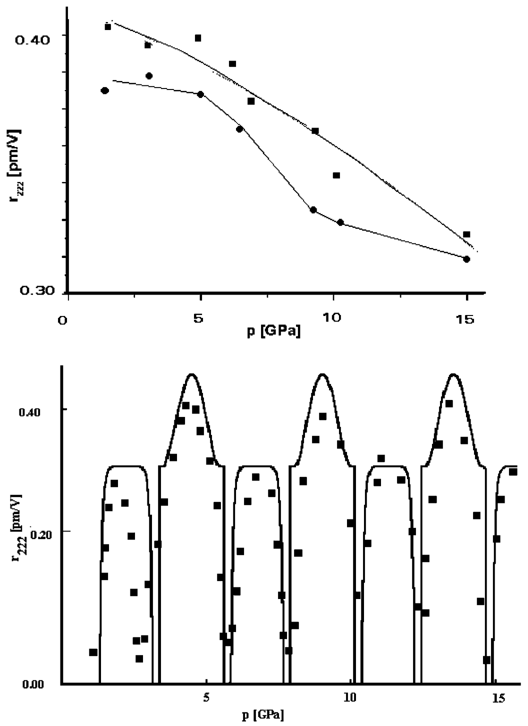


Fig. 18 LEO tensor component r_{222} coefficient *versus* pressure and temperature for pristine C_{60} at $T = 4.2$ K (■) and $T = 12$ K (●) (top) and for dyad **1Aa** at $T = 7$ K and $I = 0.5$ GW cm^{-2} (bottom).[79c] Reprinted (in part) with permission from B. Sahraoui, I. Kityk, P. Hudhomme and A. Gorgues, *J. Phys. Chem. B*, 2001, **105**, 6295, Copyright 2001, American Chemical Society.

can be clearly evidenced by steady-state and time-resolved photolysis. In the case of dyads **I**, **III**, **IV**, short-lived charge-separated radical pairs in the range of 1–2 ns were measured.[26,32,82] It was proposed as an explanation that the close proximity between the donor and the acceptor units facilitates the back electron transfer *via* formation of the fullerene triplet excited state. Comparatively, it should be noted that the excited triplet states of TTF–C_{60} dyads **1** evolve toward transient charge-separated open-shell species which present so far unexplained long-lifetimes, *i.e.* 75 μs for **1** (with R = H) and 79 μs for **1** (R = CH_3).[42b] A further development with respect to increasing the degree of stabilization of the charge-separated state consisted in extending the concept of gain of aromaticity to the gain of both aromaticity and planarity. This was clearly demonstrated by the remarkable lifetimes of the charge-separated states in C_{60}–(π-extended)TTF dyads which are in the range of 180 to 220 ns for **IX** (R = SMe and R = H respectively) in benzonitrile.[27a] Recently, for the first time, photophysical studies were carried out with the C_{60}–TTF–C_{60} triad **XI**. An efficient intramolecular electron transfer occurred evolving from the donor TTF to the singlet state of C_{60} and yielding the charge-separated radical pair with a lifetime of 88 ns in benzonitrile.[38]

Intramolecular photoinduced charge-separation and charge-recombination processes in the fused C_{60}–TTF–C_{60} dumbbell triad **2c**, which was designed to be soluble in organic solvents thanks to the substitution of C_{60} with polyalkoxy ester groups, were investigated by time-resolved absorption and fluorescence techniques.[83] Appreciable interaction between the C_{60} moiety and TTF moiety in the ground state was suggested by steady-state absorption spectra and the fluorescence spectra evidenced considerable interaction in the singlet excited state. The observed short fluorescence lifetimes of C_{60}–TTF–C_{60} compared with methanofullerene **20** in benzonitrile indicated that the charge-separation takes place *via* the singlet excited state of the C_{60} moiety, producing the ion-pair C_{60}–$TTF^{\bullet+}$–$C_{60}{}^{\bullet-}$. The lifetime of the excited singlet state of C_{60}–TTF–C_{60}, for which the energy level could be evaluated at 1.72 eV from the fluorescence peak, is in agreement with that observed in benzonitrile for the triad **XI** in which the donor TTF and acceptors C_{60} are connected through a flexible linkage.[38]

The energy level of the ion-pair state could be estimated from the first reduction potential (−0.88 V *vs.* Ag/AgCl) and the first oxidation potential (0.62 V *vs.* Ag/AgCl) (Table 2) using the centre-to-centre distance (R_{cc} = 9.2 Å) (Fig. 3). Thus, the energy diagram can be illustrated as shown in Fig. 19. The 532 nm laser excitation (2.32 eV) pumps up C_{60}–TTF–C_{60} to its singlet excited energy, from which the charge separation takes place quite efficiently in benzonitrile. A small part of the singlet states of the C_{60} moiety is converted into the triplet state of the C_{60} moiety in C_{60}–TTF–C_{60}, whose energy level is about

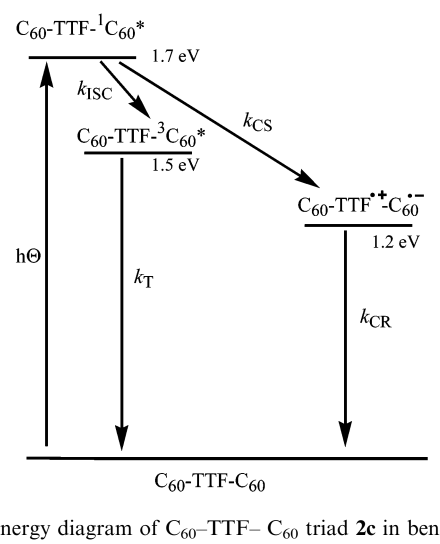


Fig. 19 Energy diagram of C_{60}–TTF– C_{60} triad **2c** in benzonitrile.

1.5 eV. After the charge separation, the charge recombination of the ion-pair occurs, returning to the ground state in benzonitrile, since the ion-pair levels are lower than the triplet state of the C_{60} moiety. The nanosecond transient absorption spectra indicated that the C_{60}–TTF–C_{60} dumbbell **2c** presents a lifetime of *ca.* 20 ns in benzonitrile which has to be compared with this observed for the ion-pair state of C_{60}–TTF–C_{60} triad **XI** (88 ns).

Conclusion

A new orientation in donor–acceptor assemblies involving tetrathiafulvalene and [60]fullerene was developed. The cyclohexene ring which constitutes a rigidified linker was considered in order to control the through-space orientation between these electroactive units. Straightforward syntheses of 2-oxo(or 2-thioxo or 2-selenoxo)-1,3-dithiole-C_{60} systems, TTF–C_{60} dyads and $(TTF)_n$–C_{60} polyads as well as the unprecedented dumbbell C_{60}–TTF–C_{60} were carried out by [4+2] Diels–Alder cycloaddition reactions. The key step consists in the preparation of versatile bis or tetrakis(bromomethylated) derivatives which could undergo the corresponding transient *o*-quinodimethane hetero-analogues *via* a reductive elimination process. Besides some examples of monoadducts TTF–C_{60} and diadducts $(TTF)_2$-C_{60} in which the tetrathiafulvalene core was substituted by alkyl- or polyalkyloxysulfanyl groups, we prepared in significant yields several unprecedented tri- and tetraadducts. Moreover, the synthesis and characterization of the dumbbell were achieved and the problem of its insolubility was partially solved by introducing solubilizing groups on [60]fullerene. Electrochemical and optical properties were performed on neutral and oxidized molecules. In particular, radical cations and radical anions derived from these polyads and triads were obtained and characterized, the latter displaying outstanding persistences. Although no significant electronic interaction was found between the electroactive species in the ground state, an efficient intramolecular electron transfer occurred in the excited state resulting in the formation of significant long-lived charge-separated state in the case of the soluble dumbbell **2c**. This suggested that the specific topology of these assemblies, characterized by their rigid conformation and the close proximity between electroactive units does not constitute a handicap to the efficient electron transfer process. These findings suggest that TTF–C_{60} or C_{60}–TTF–C_{60} systems are promising candidates for the preparation of devices for the conversion of solar energy. In fact, we are currently working on the preparation of photovoltaic cells using such assemblies.

Experimental

The following chemicals were obtained commercially and were used without any purification. C_{60} was purchased from MER company (US) and *o*-dichlorobenzene (HPLC grade) from Aldrich. Dry solvents were obtained by distillation over suitable dessicants (THF from Na/benzophenone, toluene from Na, CH_2Cl_2 from P_2O_5, CH_3CN from CaH_2). Thin-layer chromatography (TLC) was performed on aluminium sheets coated with silica gel 60 F_{254} (Merck 5735). Column chromatography was carried out on silica gel Merck 9385 Kieselgel 60 (230–400 mesh) or Florisil (Acros, 100–200 mesh). Melting points were determined using a microscope RCH (C. Reichert) with a Kofler hot stage and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on the Brucker AVANCE DRX 500 spectrometer (^1H: 500.13 MHz; ^{13}C: 125.75 MHz). Chemical shifts are reported as δ values in ppm downfield from internal TMS. Mass spectra were recorded on a VG-Autospec EBE (VG Analytical, Manchester, UK) spectrometer for FAB and EI techniques. *m*-Nitrobenzyl alcohol (*m*-NBA) was used as matrix for FAB technique. MALDI-TOF mass spectra were recorded on a Kratos spectrometer. The different matrixes used were 9-nitroanthracene (9-NA), 9,10-dimethylanthracene (9,10-DMA), dithranol (DTN). Mass spectrometry analyses were also performed using a JMS-700 (Jeol, Akishima, Tokyo) double-focusing mass spectrometer with reversed geometry, equipped with an assisted electrospray ionization (ESI) source. Cyclic voltammetry was performed in a three-electrode cell equipped with a platinum millielectrode of 7.85×10^{-3} cm^2 area and a platinum wire counter electrode. An Ag/AgCl electrode was used as reference. The electrolytic media involved *o*-dichlorobenzene (HPLC grade) and 5×10^{-1} mol L^{-1} of tetrabutylammoniumhexafluorophosphate (TBAHP-Fluka puriss quality). All experiments were carried out in solutions previously deareated by argon bubbling at 298 ± 0.5 K. Electrochemical experiments were carried out with an EGG PAR 273 A potentiostat with positive feedback compensation. UV-visible and near-IR experiments have been performed with a Perkin-Elmer Lambda 19 NIR spectrometer. HPLC experiments were performed on a Shimadzu SCL-10A VP apparatus using a reversed-phase KROMASIL 100 analytical column and HPLC grade solvents. EPR spectra were recorded on an X-Band spectrophotometer Brucker ESP 300E, equipped with a temperature controller ER412HT. Steady-state absorption spectra in the visible and near-IR regions were measured on a Jasco V570 DS spectrophotometer. Steady-state fluorescence spectra were measured on a Shimadzu RF-5300 PC spectrofluorophotometer equipped with a photomultiplier tube having high sensitivity in the 700–800 nm region. The time-resolved fluorescence spectra were measured by a single-photon counting method using a second harmonic generation (SHG, 410 nm) of a Ti:sapphire laser (Spectra-Physics, Tsunami 3950-L2S, 1.5 ps fwhm) and a streakscope (Hamamatsu Photonics, C43334-01) equipped with a polychromator (Action Research, SpectraPro 150) as an excitation source and a detector, respectively. Lifetimes were evaluated with software attached to the equipment. Nanosecond transient absorption measurements were carried out using SHG (532 nm) of a Nd:YAG laser (Spectra-Physics, Quanta-Ray GCR-130, 6 ns fwhm) as an excitation source. For transient absorption spectra in the near-IR region (600 ~ 1200 nm) and the time-profiles, monitoring light from a pulsed Xe-lamp was detected with a Ge-APD (Hamamatsu Photonics, B2834). For spectra in the Vis region (400 ~ 1000 nm), a Si-PIN photodiode (Hamamatsu Photonics, S1722-02) was used as the detector.

1,2-Cyclohexenyl-(2-oxo-1,3-dithiole)-[60]fullerene (3a)

To a mixture of C_{60} (100 mg, 0.14 mmol), dried potassium iodide (70 mg, 0.42 mmol), 18-crown-6 (369 mg, 1.4 mmol) and 5 g of 4 Å molecular sieve in dry toluene (100 mL) was added compound **8a** (42 mg, 0.14 mmol). The reaction mixture was stirred under a nitrogen atmosphere and in the dark for 48 h at room temperature. The solution was filtered on celite, washed successively with an aqueous solution of $Na_2S_2O_3$ 0.2 M (2 × 150 mL) and water (5 × 50 mL). After evaporation of the solvent, the residue was purified by silica gel column chromatography (CS_2 as the eluent). Unreacted C_{60} ($R_f = 0.89$) was separated from the monoadduct **3a** which was obtained as a brown powder in 45% yield (54 mg). m.p. > 300 °C; (^1H NMR 500 MHz, *o*-$C_6D_4Cl_2$) δ: 4.33 (4H, s); ^{13}C NMR (125 MHz, *o*-$C_6D_4Cl_2$) δ: 40.99 (CH_2), 66.53 (Csp^3 C_{60}), 136.21, 140.69, 142.09, 142.54, 142.64, 143.07, 143.52, 145.06, 145.24, 145.96, 146.02, 146.13, 146.74, 147.03, 148.18, 155.27 (Csp^2 C_{60} and SC=CS), 191.45 (C=O); IR (KBr) cm^{-1}: 527 and 1431 (C_{60}), 1642 (S–CO–S), 1658 (C=C); UV-Vis (toluene) nm: 434 , 700 ([6,6]-junction of C_{60}); MS (FAB (−), *m*-NBA) *m*/*z* (*I*%): 864 (39, M^-), 720 (100).

Diadduct. R_f (toluene) = 0.41 [R_f (toluene) monoadduct **3a** = 0.62]; MS (FAB (−), *m*-NBA) *m*/*z* (*I*%): 1008 (M^-, 24), 864 (**3a**, 16); 720 (100).

Triadduct. R_f (toluene) = 0.09 (eluted using a mixture of solvents: toluene/acetone 9 : 1); MS (FAB (−), *m*-NBA) *m*/*z* (*I*%): 1152 (M^-, 16); 1008 (diadduct, 9); 864 (monoadduct, 13); 720 (100).

1,2-Cyclohexenyl-(2-thioxo-1,3-dithiole)-[60]fullerene (3b)

This compound was prepared according to the procedure used for **3a**. Brown powder; R_f (CS_2) = 0.34; m.p. > 300 °C; ^{1}H NMR (500 MHz, *o*-$C_6D_4Cl_2$) δ: 4.30 (4H, s); ^{13}C NMR (125 MHz, *o*-$C_6D_4Cl_2$) δ: 40.93 (CH_2), 66.22 (Csp^3 C_{60}), 136.16, 139.31, 140.70, 142.09, 142.54, 142.58, 143.09, 145.04, 145.12, 146.02, 146.74, 147.05, 148.18, 154.99 (Csp^2 C_{60} and SC=CS), 210.82 (C=S); IR (KBr) cm^{-1} : 527 and 1429 (C_{60}); 1050 (C=S); 1646 (C=C); UV-Vis (toluene) *nm*: 435, 700 ([6,6]-junction of C_{60}); MS (FAB (−), *m*-NBA) *m*/*z* (*I*%): 880 (M^-, 18); 720 (100).

1,2-Cyclohexenyl-(2-selenoxo-1,3-dithiole)-[60]fullerene (3c)

This compound was prepared according to the procedure used for **3a**. The second route used the conversion of the thioxo derivative **3b** into **3c**: to a solution of selenium (98 mg) in 20 mL of water was added portionwise under vigorous stirring sodium borohydride (94 mg). The reaction mixture was stirred until the solution became clear. Toluene (40 mL), acetic acid (4 mL) and 1,3-dithiolium salt **15** (130 mg, 0.12 mmol) were successively added. After stirring for 3 h, the reaction mixture was diluted with toluene (100 mL). The organic layer was washed with a saturated aqueous solution of sodium carbonate (2 × 100 mL), then water (3 × 100 mL). After evaporation of the solvent under vacuum (without heating), the residue was chromatographed on silica gel (CS_2 as the eluent) to afford 66 mg of compound **3c** (yield = 59%); Compound **3a** was also isolated in 15–20% yield.

(3c). Brown orange powder; R_f (CS_2) = 0.28; m.p. > 300 °C; ^{1}H NMR (500 MHz, *o*-$C_6D_4Cl_2$) δ: 4.29 (4H, s); ^{13}C NMR (125 MHz, *o*-$C_6D_4Cl_2$) δ: 40.91 (CH_2), 65.95 (Csp^3 C_{60}), 136.03, 139.17, 140.51, 141.89, 142.51, 142.56, 143.08, 145.07, 145.09, 145.98, 146.74, 147.06, 148.18 and 154.74 (Csp^2 C_{60} and SC=CS), 202.77 (C=Se); IR (KBr) cm^{-1}: 525 and 1422 (C_{60}); 940 (C=Se); 1646 (C=C); UV-Vis (toluene) nm: 433, 700 ([6,6]-junction of C_{60}); MS (FAB (−), *m*-NBA) *m*/*z* (*I*%): 928 (M^-, 17); 720 (100).

1,2-Cyclohexenyl-(1,3-dithiolium)-[60]fullerene hydrogenosulfate (14a)

To a solution of 38 mg (46 μmol) of thioxo derivative **3b** in *o*-dichlorobenzene (10 mL) was added 36 mg of *m*-CPBA 66.6%. After stirring for 2 h, the precipitate was filtered, washed with toluene, water, acetone then dichloromethane to afford 32 mg of salt **14a** (yield = 78%); m.p. > 300 °C; IR (KBr) cm^{-1} : 527 and 1425 (C_{60}), 1057 and 1190 ($HSO_4{}^-$), 1640, 3200 (broad, OH); 1646 (C=C); MS (FAB (+), *m*-NBA) *m*/*z* (*I*%): 849 ([M − 97 ($HSO_4{}^-$)]$^+$, 46), 720 (100).

1,2-Cyclohexenyl-(1,3-dithiolium)-[60]fullerene hexafluorophosphate (14b)

This compound was prepared according to the procedure used for the 1,3-dithiolium salt **14a**, except that the reaction was carried out in a saturated solution of tetrabutylammonium hexafluorophosphate in *o*-dichlorobenzene. 32 mg of brown powder were isolated (yield = 70%); m.p. > 300 °C; IR (KBr) cm^{-1} : 527 and 1426 (C_{60}), 841 ($PF_6{}^-$); 1646 (C=C); MS (FAB (+), *m*-NBA) *m*/*z* (*I*%): 849 ([M −145 ($PF_6{}^-$)]$^+$, 41), 720 (100).

1,2-Cyclohexenyl-(1,3-dithiolium)-[60]fullerene tetrafluoroborate (14c)

First method: this compound was prepared according to the procedure used for 1,3-dithiolium salt **14a**, except that after 30 min of reaction, 62 μl of tetrafluoroboric acid in ether (54% weight) was added. The reaction mixture was then stirred for 24 h. The precipitate was washed with water, toluene, then dichloromethane to afford 30 mg (yield = 70%) of salt **14c**. Second method: to a solution of 23 mg (25 μmol) of compound **16** in acetic anhydride (25 mL) was added dropwise at 0 °C 35 μl of tetrafluoroboric acid in ether (54 wt%). After stirring for 8 h, the solution was refrigerated overnight. The precipitate was filtered, washed successively with water, acetone, toluene, then dichloromethane to afford 24 mg (yield = 56%) of salt **14c**; m.p. > 300 °C; IR (KBr) cm^{-1} : 526 (C_{60}), 1033 and 1051 ($BF_4{}^-$); MS (FAB (+), *m*-NBA) *m*/*z* (*I*%): 849 ([M −87 ($BF_4{}^-$)]$^+$, 39), 720 (100).

1,2-Cyclohexenyl-(2-methylsulfanyl-1,3-dithiolium)-[60]fullerene trifluoromethanesulfonate (15)

Methyl trifluoromethanesulfonate (300 μL) was added at room temperature to a solution of thione **3b** (29 mg, 33 μmol) in 20 mL of dry toluene. After stirring overnight at room temperature, the precipitate was filtered, washed with toluene, water then acetone. The product was dried under vacuum to yield the dithiolium salt **15** (32 mg, yield = 94%) as brown powder; IR (KBr) cm^{-1} : 527 (C_{60}), 1031 and 1163 ($SO_3{}^-$), 1428 and 2870 (S–Me); MS (FAB (+), *m*-NBA) *m*/*z* (*I*%): 895 ([M −149 ($CF_3SO_3{}^-$)]$^+$, 37), 720 (100).

1,2-Cyclohexenyl-(2-methylsulfanyl-1,3-dithiole)-[60]fullerene (16)

To a suspension of 40 mg (38 μmol) of salt **15** in 20 mL of anhydrous toluene was slowly added 72 mg of sodium borohydride. After stirring for 24 h, the solution was filtered, washed with water (3 × 40 mL). The organic layer was dried and the solvent was evaporated to afford 27 mg (yield = 81%) of compound **16**; R_f (CS_2) = 0.53; m.p. > 300 °C; ^{1}H NMR (500 MHz, CS_2 + ε $CDCl_3$) δ: 2.40 (s, 3H, CH_3), 3.30 (s, 1H, CH), 4.30 (t, 4H, CH_2); IR (KBr) cm^{-1}: 525 (C_{60}), 1056 and 1065 (C–S), 1461 (S–Me), 1641 (C=C), 2853 (S–CH); UV-Vis (toluene) nm: 432, 700 ([6,6]-junction of C_{60}); MS (FAB (−), *m*-NBA) *m*/*z* (*I*%): 896 ($M^{\bullet-}$, 19); 720 (100).

1,2-Cyclohexenyl-[bis(methylsulfanyl)tetrathiafulvalene]-[60]fullerene (1Aa)

A mixture of the corresponding bis(bromomethyl)-TTF **9** (235 mg, 0.49 mmol), C_{60} (351 mg, 0.49 mmol), 18-crown-6 (1.03 g, 3.92 mmol) and anhydrous potassium iodide (179 mg, 1.08 mmol) in dry toluene (200 mL) was stirred under a nitrogen atmosphere for 48 h at room temperature in the dark. After work-up and silica gel column chromatography (CS_2), 205 mg of monoadduct **1Aa** was isolated as brown crystalline powder (40% yield); R_f (CS_2) = 0.39; m.p. > 300 °C; ^{1}H NMR (500 MHz, *o*-$C_6D_4Cl_2$) δ: 2.37 (s, 6H, SCH_3), 4.33 (s, 4H, CH_2); IR (KBr) cm^{-1}: 512, 527, 575, 697, 775 and 1427 (C_{60}), 1183, 1257 (SCH_3), 1385, 1510 and 1685 (C=C), 2847, 2915 and 2958 (SCH_3); UV-Vis (toluene) nm: 262, 320, 434, 515 and 701 [6,6]-junction of C_{60}); MS (MALDI, DTN-CH_2Cl_2) *m*/*z*: 1042 ($M^{+\bullet}$).

Diadduct (1Ba). Brown powder; R_f (CS_2) = 0.23; this compound is eluted using CS_2/acetone (95 : 5); m.p. > 300 °C;

IR (KBr) cm^{-1}: 526, 575, 618, 638, 773 and 1428 (C_{60}), 1129, 1183, 1686 (C=C); UV-Vis (toluene) *nm*: 250, 320, 434, 516 and 701 [6,6]-junction of C_{60}); MS (MALDI, DTN-CH_2Cl_2) *m*/*z*: 1364 ($M^{+\bullet}$), 1091, 1042 (**1Aa**).

Triadduct (1Ca). Brown powder; R_f (CS_2/acetone 95 : 5) = 0.18; this compound is eluted using CS_2/acetone (9 : 1); m.p. > 300 °C; IR (KBr) cm^{-1}: 527, 574, 773 and 1427 (C_{60}), 1183, 1685 (C=C); UV-Vis (toluene) *nm*: 248, 319, 435, 516 and 702 [6,6]-junction of C_{60}; MS (MALDI, DTN-CH_2Cl_2) *m*/*z*: 1686 ($M^{+\bullet}$), 1364 (**1Ba**), 1042 (**1Aa**).

1,2-Cyclohexenyl-[bis(pentylsulfanyl)tetrathiafulvalene]-[60]fullerene (1Ab)

This compound was prepared according to the procedure used for **1Aa**. (**1Ab**). Brown powder; R_f (CS_2) = 0.74; m.p. = 190 °C (dec.); ^{1}H NMR (500 MHz, CS_2 + ε C_6D_6) δ: 0.85 (t, 6H, CH_3), 1.20–1.30 (m, 8H, $–C\underline{H}_2–C\underline{H}_2–CH_3$), 1.55 (m, 4H, $–S–CH_2–C\underline{H}_2$), 2.70 (t, 4H, $S–C\underline{H}_2$), 4.17 (s, 4H, $C=C–C\underline{H}_2$); ^{13}C NMR (125 MHz, CS_2 + ε C_6D_6) δ 14.83 (2C, CH_3), 23.20 (2C, $CH_3–\underline{C}H_2–$), 30.15 (2C, $–S–CH_2–\underline{C}H_2$), 31.43 (2C, $CH_3–CH_2–\underline{C}H_2–$), 36.93 (2C, $–S–\underline{C}H_2–$), 41.24 (2C, $–C=C–\underline{C}H_2$, 66.06 (Csp^3 C_{60}), 109.49 and 113.28 (2C, C=C ylidene), 127.81 and 128.58 (4C, C=C), 136.07 to 147.85 (Csp^2 C_{60}), 155.18 (2C, $\underline{C}sp^2–Csp^3$ C_{60}); IR (KBr) cm^{-1} : 527, 575, 775 and 1422 (C_{60}), 718 ($C–CH_2–C$), 1183, 1462 (SCH_2), 1685 (C=C); UV-Vis (toluene) nm: 263, 321, 434, 515 and 701 [6,6]-junction of C_{60}); MS (MALDI (−), 9-NA-toluene) *m*/*z*: 1153 ($[M - 1]^-$).

Diadduct (1Bb). Brown powder; R_f (CS_2) = 0.40; m.p. = 163 °C (dec.); ^{1}H NMR (500 MHz, CS_2 + ε C_6D_6) δ: 0.70–1.00 (m, 12H, CH_3), 1.10–1.38 (m, 16H, $C\underline{H}_2C\underline{H}_2\,CH_3$), 1.41–1.61 (m, 8H, $SCH_2–C\underline{H}_2$), 2.57–2.70 (m, 8H, SCH_2), 3.61–4.42 (m, 8H, $C=C–CH_2$); UV-Vis (toluene) nm: 250, 317, 435, 516 and 702 [6,6]-junction of C_{60}); MS (MALDI (−), 9-NA-toluene) *m*/*z*: 1588 (M^-), 1326, 1154 (**1Ab**).

Triadduct (1Cb). Brown powder; R_f (CS_2) = 0.19; this compound is eluted using CS_2/acetone (98 : 2); m.p. = 114 °C; UV-Vis (toluene) nm 247, 318, 435, 515 and 701 [6,6]-junction of C_{60}; MS (MALDI (−), 9,10-DMA, toluene) *m*/*z*: 2022 (M^-), 1588 (**1Bb**), 1154 (**1Ab**).

Tetraadduct (1Db). Brown powder; R_f (CS_2/acetone 98 : 2) = 0.26; this compound is eluted using CS_2/acetone (95 : 5); m.p. = 88 °C (dec.); UV-Vis (toluene) nm: 262, 321, 435, 515 and 703 [6,6]-junction of C_{60}; MS (MALDI, DTN–CH_2Cl_2) *m*/*z*: 2456 (M^+), 2022 (**1Cb**), 1588 (**1Bb**), 1154 (**1Ab**).

1,2-Cyclohexenyl-[bis(octylsulfanyl)tetrathiafulvalene]-[60]fullerene (1Ac)

This compound was prepared according to the procedure used for 1**Aa**. (**1Ac**): Brown powder; R_f (CS_2/petroleum ether 7 : 3) = 0.71; m.p. = 114 °C (dec.); ^{1}H NMR (500 MHz, CS_2 + ε C_6D_6) δ: 0.83 (t, 6H, CH_3), 0.98–1.62 (m, 24H, $(C\underline{H}_2)_6CH_3$, 2.69 (t, 4H, SCH_2), 4.14 (s, 4H, $C=C-CH_2$); IR (KBr) cm^{-1} : 527, 776 and 1423 (C_{60}), 719 ($C–CH_2–C$), 1462 (SCH_2), 1686 (C=C); UV-Vis (toluene) nm: 434, 515 and 701 [6,6]-junction of C_{60}); MS (MALDI, DTN–CH_2Cl_2) *m*/*z*: 1238 (M^+).

1,2-Cyclohexenyl-[bis(dodecylsulfanyl)tetrathiafulvalene]-[60]fullerene (1Ad)

This compound was prepared according to the procedure used for **1Aa**. (**1Ad**). Brown powder; R_f (CS_2) = 0.79; this compound is eluted using CS_2/petroleum ether (8 : 2) with 1% of Et_3N; m.p. = 126 °C (dec.); ^{1}H NMR (500 MHz, CS_2 + ε C_6D_6) δ: 0.83 (t, 6H, CH_3), 1.11–1.38 (m, 36H, $(C\underline{H}_2)_9CH_3$, 1.54 (m, 4H, $SCH_2–C\underline{H}_2$), 2.69 (t, 4H, SCH_2), 4.11 (s, 4H, $C=C-CH_2$); IR (KBr) cm^{-1} : 508, 529, 559, 578, 699, 722, 773 and 1428 (C_{60}), 893, 1303, 1472 (SCH_2), 1685 (C=C); UV-Vis (toluene) nm: 434, 515 and 701 [6,6]-junction of C_{60}); MS (MALDI, 9-NA–toluene) *m*/*z*: 1350 (M^+).

1,2-Cyclohexenyl-(ethylenedisulfanyltetrathiafulvalene)-[60]fullerene (1Ae)

This compound was prepared according to the procedure used for **1Aa**. (**1Ae**). Brown powder; R_f (CS_2) = 0.41; m.p. > 300 °C; ^{1}H NMR (500 MHz, CS_2 + ε C_6D_6) δ: 3.10–3.55 (m, 4H, SCH_2CH_2S), 4.34–4.78 (m, 4H, $C=C–CH_2$); IR (KBr) cm^{-1}: 512, 527, 696, 766, 773 and 1423 (C_{60}), 1182, 1254 (SCH_2), 1508 (C=C), 2848, 2912 and 2956 (CH_2); UV-Vis (toluene) nm: 262, 322, 434, 515 and 701 [6,6]-junction of C_{60}); MS (MALDI (−), 9-NA–toluene) *m*/*z*: 1040 (M^+).

Diadduct (1Be). Brown powder; R_f (CS_2/acetone 95 : 5) = 0.42 [R_f(**1Ae**) = 0.63]; this compound is eluted using CS_2/acetone (9 : 1); m.p. > 300 °C; IR (KBr) cm^{-1} : 512, 527, 765, 773 and 1426 (C_{60}), 1254 (SCH_2), 1508 (C=C), 1684, 2845, 2911 and 2957 (CH_2); UV-Vis (toluene) nm: 250, 320, 434 and 700 [6,6]-junction of C_{60}); MS (MALDI , DTN–CH_2Cl_2) *m*/*z*: 1360 (M^+), 1214, 1185, 1040 (**1Ae**).

Triadduct (1Ce). Brown powder; this compound is eluted using CS_2/acetone (85 : 15) [R_f (CS_2/acetone 9 : 1) = 0.27 [R_f (**1Be**) = 0.56]; m.p. > 300 °C; IR (KBr) cm^{-1}: 473 (broad), 527, 773 and 1426 (C_{60}), 804, 1100 (broad), 1254 (SCH_2), 1508 (C=C), 1684, 2848, 2913 and 2959 (CH_2); UV-Vis (toluene) nm : 250, 320, 434, 515 and 702 [6,6]-junction of C_{60}; MS (MALDI, DTN–CH_2Cl_2) *m*/*z*: (M^-absent), 1391, 1360 (**1Be**), 1040 (**1Ae**).

1,2-Cyclohexenyl-[bis(3,6,9-trioxadecylsulfanyl)-tetrathiafulvalene]-[60]fullerene (1Af)

This compound was prepared according to the procedure used for **1Aa**. (**1Af**). Brown crystalline powder; this compound is eluted using CS_2/acetone/Et_3N (88 : 10 : 2); R_f (CS_2/acetone 9 : 1) = 0.23 [R_f (C_{60}) = 0.99]; m.p. = 82 °C (dec); ^{1}H NMR (500 MHz), $CDCl_3$) δ: 3.07 (t, 4H, SCH_2), 3.39 (s, 6H, OCH_3), 3.57 (m, 4H, $C\underline{H}_2–OMe$), 3.67 (m, 12H, OCH_2), 3.72 (t, 4H, $SCH_2–C\underline{H}_2O$), 4.32 (s, 4H, $C=C–CH_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 35.66 (2C, SCH_2), 41.17 ($C=C–\underline{C}H_2$), 59.04 ($O\underline{C}H_3$), 66.08 (Csp^3 C_{60}), 70.21 ($SCH_2–\underline{C}H_2O$), 70.68 and 70.70 (12C, CH_2O), 72.09 (2C, $\underline{C}H_2–OCH_3$), 108.13 and 113.84 (2C, C=C ylidene), 128.32 and 128.50 (4C, C=C), 135.82 to 147.84 (Csp^2 C_{60}), 155.30 (2C, $\underline{C}sp^2–Csp^3$ C_{60}); IR (KBr) cm^{-1}: 527, 576 and 775 (C_{60}), 1037, 1106 ($CH_2–O–CH_2$), 1201, 1487, 1513, 1601 (C=C); UV-Vis (CH_2Cl_2) nm: 260, 326, 434, 510 and 701 [6,6]-junction of C_{60}); MS (MALDI , DTN–CH_2Cl_2) *m*/*z*: 1306 (M^+).

Diadduct (1Bf). Brown solid; this compound is eluted using CS_2/acetone/Et_3N (82 : 16 : 2); R_f (CS_2/acetone 85 : 15) = 0.29 [R_f(**1Af**) = 0.64]; m.p. = 90 °C (dec); UV-Vis (CH_2Cl_2) *nm* : 249, 321, 434, 509 and 701 [6,6]-junction of C_{60}); MS (MALDI, DTN–CH_2Cl_2) *m*/*z*: ($M^{+\bullet}$ absent), 1706, 1524, 1306 (**1Af**).

Triadduct (1Cf). Brown powder; this compound is eluted using CS_2/acetone/Et_3N (82 : 16 : 2); [R_f (CS_2/acetone 8 : 2) = 0.29 [R_f (**1Bf**) = 0.38)]; m.p. = 104 °C (dec.); UV-Vis (CH_2Cl_2) nm: 250, 320, 435, 510 and 702 [6,6]-junction of C_{60}; MS (MALDI, DTN–CH_2Cl_2) *m*/*z*: (M^-absent), 1888 (**1Bf**), 1740, 1706, 1524, 1306 (**1Af**).

Tetraadduct (1Df). Brown powder; this compound is eluted using CS_2/acetone/Et_3N (70 : 28 : 2); [R_f (CS_2/acetone 7 : 3) = 0.31 [R_f (**1Cf**) = 0.58)]; m.p. = 123 °C (dec.); UV-Vis (CH_2Cl_2) *nm*: 435, 510 and 701 [6,6]-junction of C_{60}; MS (MALDI, DTN–CH_2Cl_2) *m*/*z*: (M^-absent), 1306 (**1Af**).

1,2-Cyclohexenyl-[bis(3,6,9,12-tetraoxatridecylsulfanyl)-tetrathiafulvalene]-[60]fullerene (1Ag)

This compound was prepared according to the procedure used for **1Aa**. (**1Ag**). Deep brown crystalline solid; this compound is eluted using CS_2/acetone/Et_3N ((85 : 13 : 2); R_f (CS_2/acetone 85 : 15) = 0.37; m.p. = 71 °C (dec); ^1H NMR (500 MHz, $CDCl_3$) δ: 3.06 (t, 4H, SCH_2), 3.38 (s, 6H, OCH_3), 3.56 (m, 4H, $C\underline{H}_2$–OMe), 3.59–3.76 (m, 24H, OCH_2), 4.32 (s, 4H, C=C–CH_2); IR (KBr) cm^{-1}: 527, 576, 698 and 775 (C_{60}), 1023, 1108 (CH_2–O–CH_2), 1201, 1487, 1513, 1601 (C=C); UV-Vis (CH_2Cl_2) nm: 261, 325, 434, 510 and 701 [6,6]-junction of C_{60}); MS (MALDI, 9,10-DMA–toluene) *m*/*z*: 1394 ($M^{+\cdot}$), 849, 847.

Diadduct (1Bg). Deep brown solid; this compound is eluted using CS_2/acetone/Et_3N ((8 : 18 : 2); R_f (CS_2/acetone 8 : 2) = 0.25 [R_f (**1Ag**) = 0.37]; m.p. = 81 °C (dec); UV-Vis (CH_2Cl_2) nm : 251, 321, 434, 509 and 702 [6,6]-junction of C_{60}); MS (MALDI, DTN–CH_2Cl_2) *m*/*z*: (M^+ absent), 1706, 1394 (**1Ag**).

Triadduct (1Cg). Deep brown solid; this compound is eluted using CS_2/acetone/Et_3N (75 : 23 : 2); [R_f (CS_2/acetone 8 : 2) = 0.18; m.p. = 93 °C (dec.); UV-Vis (CH_2Cl_2) nm: 248, 322, 435 and 701 [6,6]-junction of C_{60}; MS (MALDI, DTN–CH_2Cl_2) *m*/*z*: (M^- absent), 2068 (**1Bg**), 1706, 1394 (**1Ag**).

Dumbbell (2a). A solution of freshly prepared tetrakis-(bromomethyl)TTF **10** (300 mg, 0.52 mmol), C_{60} (751 mg, 1.04 mmol), 18-crown-6 (1.34 g, 5.1 mmol) and anhydrous potassium iodide (521 mg, 3.14 mmol) in HPLC grade *o*-dichlorobenzene (400 mL) was stirred under a nitrogen atmosphere for 48 h at room temperature in the dark. The precipitate was filtered, washed successively with CS_2 (100 mL), an aqueous solution of $Na_2S_2O_3$ 1 M (15 mL), water (25 mL), acetone (50 mL), methanol (50 mL), then dichloromethane (50 mL). The product was dried under vacuum (yield = 30 to 45%). A second crop was obtained after addition of dichloromethane (800 mL) to the *o*-dichlorobenzene solution. The precipitate was filtered and similar treatments were carried out affording 15 to 20% of supplementary material; m.p. > 300 °C; IR (KBr) cm^{-1} : 527 (C_{60}), 767 (C–S), 1429 (C=C), UV-Vis (*o*-$C_6H_4Cl_2$) nm: 435 and 700 [6,6]-junction of C_{60}); MS (MALDI, DTN–toluene) *m*/*z*: 1696 (M^+), 976 ($[M - C_{60}]^+$), 847 ($[M/2 - H]^+$), 720 ($C_{60}{}^{+}$); MS (FAB (+) *m*/*z* (*I*%): 256; MS (ESI+): Calcd mass = 1695.9509; found = 1695.9550.

Dumbbell (2b). This compound was prepared according to the procedure used for **2a**; after work-up, dumbbell **2b** was purified by column chromatography on florisil (CS_2/Et_3N/acetone 90 : 5 : 5), m.p. > 300 °C; ^1H NMR (500 MHz, $CDCl_3$) δ: 1.21–2.05 (m, 12H, CH_3), 3.71–5.10 (broad m, 16H, CH_2 and OCH_2); IR (KBr) cm^{-1}: 526 and 766 (C_{60}), 1093 (C–S), 1231 (C–O–C), 1442 (C=C), 1738 (C=O); UV-Vis (CH_2Cl_2) nm: 445, 704 ([6,6]-junction of C_{60}); MS (MALDI, 9,10-DMA–toluene) *m*/*z*: 1134 ([M − **19**]$^+$), 1005 ($[M/2 - H]^+$), 878 (**19** $^+$), 720 ($C_{60}{}^{+}$); MS (FAB (+) *m*/*z* : 256; MS (ESI+): Calcd mass = 2012.0667; found = 2012.0647.

Bis(3,6,9-trioxadecyloxycarbonyl)methanofullerene (20)

To a mixture of 0.238 g of di(3,6,9-trioxadecyl) malonate (0.6 mmol), 0.432 g of C_{60} (0.6 mmol) and 0.199 g of carbon tetrabromide (0.6 mmol) in 300 mL of anhydrous toluene was added 0.18 mL of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (1.2 mmol). The solution was stirred for 18 h in the dark, then was washed with an aqueous solution of sodium thiosulfate (2 × 150 mL) and water (2 × 150 mL). After evaporation of the solvent under vacuum, the residue was purified by column chromatography (silica gel, CS_2 to get rid of C_{60}, then CH_2Cl_2 and lastly CH_2Cl_2/acetone 9 : 1, R_f = 0.29). Methanofullerene **20** was isolated as a brown solid (0.307 g, yield = 46%); m.p. = 84 °C (dec.); ^1H NMR (500 MHz, $CDCl_3$) δ: 3.38 (s, 6H, $CH_2OC\underline{H}_3$), 3.55 (m, 4H, $C\underline{H}_2OCH_3$), 3.61–3.68 (m, 8H, CH_2O), 3.68–3.77 (m, 4H, CH_2O), 3.88 (m, 4H, $CO_2CH_2C\underline{H}_2O$), 4.65 (m, 4H, CO_2CH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 52.27 ($CO_2\,\underline{C}H_2$), 59.02 ($O\underline{C}H_3$), 66.26 (Csp^3 C_{60}), 68.82 (O_2C–$\underline{C}H_2$–CO_2), 70.66, 70.77, 71.58, 72.01 (CH_2O), 139.13, 140.97 (Csp^2 C_{60}), 145.36 (Csp^2 –Csp^3 C_{60}), 163.48 (C=O); IR (KBr) cm^{-1}: 527 (C_{60}), 845, 1108 (C–O), 1230, 1428, 1740 (C=O), 2870 (CH_2 and CH_3); UV-Vis (CH_2Cl_2) nm: 427; 461; 689; MS (MALDI, DTN–CH_2Cl_2) *m*/*z*: 1135 ($[M + Na]^+$).

Dumbbell (2c). To a mixture of 0.310 g of tetrakis(bromomethyl)TTF **10** (0.535 mmol) and 1.5 g of methanofullerene **20** (1.34 mmol) in 150 mL of anhydrous toluene were added 0.538 g of potassium iodide (3.24 mmol) and 1.38 g of 18-crown-6 (5.23 mmol). The solution was stirred for 48 h in the dark. The reaction mixture was filtered and the precipitate was washed successively with toluene (20 mL), an aqueous solution of sodium thiosulfate (20 mL), water (10 mL), acetone (10 mL), methanol (10 mL), then toluene (10 mL) and acetone (10 mL) again. The brown solid was dried under vacuum to furnish 0.270 g of material (yield = 20%); m.p. > 300 °C; ^1H NMR (500 MHz, $CDCl_3$) δ: 3.42 (s, 12H, $CH_2OC\underline{H}_3$), 3.50–4.28 (m, 48H, CH_2O), 4.28–5.11 (m, 8H, C–CH_2–C), IR (KBr) cm^{-1}: 527 (C_{60}), 767 (C–S), 840, 1109 (C–O), 1233, 1429 (C=C), 1742 (C=O), 2865 (CH_2 and CH_3); UV-Vis (CH_2Cl_2) nm: 358, 401, 512, 701; MS (MALDI, DTN–CH_2Cl_2) *m*/*z* : 1370 ([M − **20**]$^+$), 1243 ($[M/2 - H]^+$); 720 ($C_{60}{}^{+}$); MS (FAB (+)): 256; MS (ESI+): Calcd mass = 2484.4217; found = 2484.4238.

Dumbbell (2d). This compound was prepared according to the procedure used for **2a**; m.p. > 300 °C; IR (KBr) cm^{-1} : 527, 560, 585, 690, 1188, 1428, 1448, 1740 (CO_2Me); UV-Vis (*o*-$C_6H_4Cl_2$) nm : 445, 473, 715 ([6,6]-junction of C_{60}); MS (MALDI, DTN–CH_2Cl_2) *m*/*z*: 1166 ([M − **21**]$^+$), 1037 ($[M/2 - H]^+$); MS (ESI+): Calcd mass = 2076.1538; found = 2076.1538.

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